

**PRACTICAL GUIDE**  
*and* **SPECTRAL**  
**ATLAS** *for*  
**INTERPRETIVE**  
**NEAR-INFRARED**  
**SPECTROSCOPY**

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**SECOND EDITION**

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**SPECTROSCOPY**

**SECOND EDITION**

**Jerry Workman Jr. • Lois Weyer**



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*To inspiring teachers, professors, friends, and family and to independent thinkers everywhere.*



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# Preface

In this second edition of *Practical Guide and Spectral Atlas for Interpretive Near-Infrared Spectroscopy*, we have endeavored to expand and update the chapters, and to produce the figures in a more dramatic spectral atlas format, that is, in a four-color,  $8\frac{1}{2} \times 11$  book. The color and larger graphical presentation provides richer, more detailed spectra than the first edition. This revised atlas also includes new research, editorials, supplements, and molecular structural formulas (Appendix H), including updated references and information on near-infrared (NIR) spectra.

Qualitative and quantitative NIR spectroscopic methods require the application of multivariate calibration algorithms commonly referred to as chemometric methods to model spectral response to chemical or physical properties of a calibration, teaching, or learning sample set. The identification of unique wavelength regions where changes in the response of the NIR spectrometer are proportional to changes in the concentration of chemical components, or in the physical characteristics of samples under analysis, is required for a scientific understanding of cause (i.e., molecular or physical properties) and effect (i.e., spectroscopic changes), even for routine method development.

The first step to developing an analytical method using NIR is to measure a spectrum of the sample using an NIR spectrophotometer. It is helpful to note that the NIR spectrum obtained by using a spectrophotometer is the result of the convolution of the measuring instrument function with the unique optical and chemical characteristics of the sample measured. The sample participates as an optical element in the spectrometer. The resultant spectrum contains information specific to the molecular vibrational aspects of the sample, its physical properties, and its unique interaction with the measuring instrument. Relating the spectra to the chemical structure of the measured samples is referred to as spectra–structure correlation. This correlation or interpretation of spectra converts the abstract absorption data (spectrum) into structural information representing the molecular details about a measured sample. Interpretive spectroscopy of this sort provides a basis for the establishment of known cause-and-effect relationships between the spectrometer response (spectrum) and the molecular properties of the sample.

The exclusive use of chemometrics provides only a correlation-based framework for analytical science. When performing multivariate calibrations, analytically valid calibration models require a fundamental relationship between X (the instrument response data or spectral data) and Y (the reference data); probability tells us only if X and Y “appear” to be related. If no cause–effect relationship exists between X and Y, then the analytical method will have no true predictive significance. Interpretation of NIR spectra provides the knowledge basis for understanding the cause and effect of molecular structure as it relates to specific types of absorptions in the NIR. Interpretive spectroscopy is a key intellectual process in approaching NIR measurements if one is to achieve an analytical

understanding of these measurements. This spectral atlas represents our best effort to provide the tools necessary for the analyst to interpret NIR spectra.

This is the second edition of the only book to date written specifically on the subject of interpretation of NIR spectra. We have tried to be comprehensive by providing prodigious reference to the better known, classic reviews published on this subject. In this work we are attempting to comprehensively cover the subject matter but have oriented the book toward using the information for solving analytical problems, rather than attempting a more detailed coverage of the theory of NIR vibrational spectroscopy.

The most important early reviews covered the 1920s through the 1950s, a time when new commercial UV–Vis–NIR (ultraviolet–visible–near infrared) instruments became available, and interest in the spectral region increased in both academia and industry. These reviews included those by Wilbur Kaye<sup>1</sup> of Tennessee Eastman, Owen Wheeler at the University of Puerto Rico,<sup>2</sup> and Robert Goddu<sup>3</sup> of Hercules Powder Company (late Hercules Incorporated). In addition, Wheeler cited an earlier review by Joseph W. Ellis<sup>4</sup> summarizing NIR papers published before 1929, and Lauer and Rosenbaum reviewed band assignments in 1952.<sup>5</sup>

Wheeler's article includes a table of approximate theoretical wavelengths of overtones, such as the C–H stretch first overtone at 1.7 microns, the second overtone at 1.1 microns, the third at 0.85, and the fourth at 0.7. Kaye's 1954 article provided a chart of the spectra–structure correlations and approximate absorptivities that were available at that time. The same article also provided very detailed band assignment tables and spectra for a few specific compounds. In 1960, Goddu and Delker<sup>6</sup> published a more complete chart that has been widely reproduced. It was based on literature references and personal knowledge from a series of studies and subsequent publications.

During the 1960s and 1970s, NIR was not studied as extensively, although another important review was written by Kermit Whetsel in 1968,<sup>7</sup> and some work did continue at specific institutions. A chapter on NIR interpretation was included in Robert Conley's text on infrared spectroscopy published in 1966.<sup>8</sup> This was the time period in which Karl Norris at the U.S. Department of Agriculture (USDA) began his research that would lead to the greatly renewed interest in this spectral field, but there was initially a disconnect between the new agricultural applications of NIR and the earlier academic and chemical industry interests.

There were some specialized reviews during this time period. For example, reviews on hydrocarbon NIR spectra were written by Bernhard and Berthold,<sup>9</sup> and Tosi and Pinto.<sup>10</sup> An atlas of 1000 NIR spectra of a wide selection of general chemicals was published in 1981.<sup>11</sup> Although the spectral bands are not interpreted, the atlas provides an excellent reference collection.

As the new, rapid scan, optically optimized instruments became popular in the food and agricultural industries, and began to be noticed by other industries, several reviews were written to bridge the knowledge gap. These include those by Weyer;<sup>12</sup> Honig;<sup>13</sup> and Stark, Luchter, and Margoshes.<sup>14</sup> An important book, which was first published in 1987 by Norris and Williams, has a chapter on chemical principles including band assignments.<sup>15</sup> There is also interpretive information in Osborne and Fearn's food analysis book.<sup>16</sup> More recent extensive reviews on spectral interpretation include those by Workman,<sup>17</sup> and Weyer and Lo.<sup>18</sup>



The short-wave near-infrared spectral region was specifically discussed by Schrieve et al.<sup>19</sup> They referred to synonyms such as the “far-visible,” the “near, near-infrared,” or the “Herschel-infrared” to describe the range of approximately 700 to 1100 nm of the electromagnetic spectrum (EMS). The authors cite the increased interest of this spectral region to spectroscopists, particularly those involved with implementing process near-infrared measurements. More details regarding this spectral region are also described in a comprehensive handbook by Workman.<sup>20</sup>

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# Authors

**Jerome J. Workman, Jr., CSci, CChem, FRSC**, is a prolific author and editor of scientific reference works on the subject of spectroscopy. He is a noted spectroscopist, with training in biology and chemistry. He has published 12 reference text volumes, including the multivolume Academic Press *Handbook of Organic Compounds* and is currently commissioned to edit a five-volume reference collection on spectroscopy for World Scientific Publishers. He has published or edited major reviews and several hundred technical papers on the subject of spectroscopy. For this work he has received the Coblentz Society Williams-Wright Award, the ASTM International Award of Merit, and an Eastern Analytical Symposium Award. He, along with coauthor Howard L. Mark, has published columns on statistics and chemometrics since 1986. He has lectured widely and internationally on spectroscopy including the Oxford Conference on Spectrometry, and throughout the United States, Canada, Europe, and Asia from 1986 to the present.

He has authored 465-plus scientific papers and abstracts, and more than 125 major proprietary corporate research reports, 30 invention disclosures/patents, and 12 textbook volumes. In addition to original research in spectroscopic methods, Workman has been prolific in publishing heavily cited review works for the journals *Analytical Chemistry* and *Applied Spectroscopy Reviews* in chemometrics, process analytical chemistry, and a variety of vibrational spectroscopy topics, making him highly sought after for discussions in these fields. He often speaks about the unique uses of light technology for solving challenging and complex commercial and medical problems.

He holds a BA degree cum laude in natural sciences and MA degree in biological sciences with genetics-evolution emphasis from Saint Mary's University of Minnesota; and a PhD in biological chemistry from Columbia Pacific University. He holds four graduate certifications from Columbia University and the Massachusetts Institute of Technology. His current position is as executive vice president of engineering at Unity Scientific, where he directs research and development for commercial laboratory, process, and clinical instrumentation. He is also adjunct professor of biomedical statistics and virology at United States National University, California, and adjunct professor of biology at Liberty University, Virginia. He has held major research and executive positions in startups to large global conglomerates.

**Lois Weyer** began her industrial analytical chemist career in the UV-Vis-NIR laboratory at Hercules Incorporated and inherited the Cary 14 spectrometer upon which Robert Goddu and Dorothy Delker had done their extensive near IR work in the 1950s and 60s. Although the near IR spectral region had fallen out of favor by the 1970s, the need for justifying the purchase of a new UV-Vis-NIR instrument for the lab prompted her to explore the capabilities of the near IR region. A literature survey was done, an internal report written, and a new Cary 17 was purchased. During the course of the literature

exploration, however, Lois found that a new wave of interest in near IR spectroscopy had arisen in the food and agricultural industry. She realized that the devices developed for the rapid, direct analyses of fruits, grains, and dairy products might also be applied to industrial materials. At an international conference on the agricultural applications, she saw that most of the practitioners of the new NIR field were not aware of the spectral band interpretations. This led to another literature survey, a published review article, and justification for a Neotec 6350 spectrometer.

The new class of rapid-scan NIR instruments was ideal for chemical process analyses and Lois initiated a program to provide Hercules plants with new methods for quality control, problem solving, and process analysis. Instantaneous analyses for cellulose in blends, hydroxyl number of resins, solvents in rocket propellant, moisture and degree of substitution of cellulose and many other applications contributed to millions of dollars saved in production costs, conservation of raw materials, and probable prevention of loss of lives in explosions. Other techniques including Raman spectroscopy, filter mid-IR, UV, ultrasound, and physical property analyzers were added to this effort, and teams of chemists and engineers were developed to install process analysis systems in chemical plants throughout the world. In conjunction with this effort, Lois completed a number of external papers, many internal publications, a patent and several disclosures of invention, and many presentations at international conferences. She has also taught short courses in near IR spectroscopy and process analysis for many years.

She holds a BA degree in chemistry from Douglass College of Rutgers University, an MS in physical chemistry from the University of Delaware, and earned a PhD in analytical chemistry in 1996 at the University of Delaware while working fulltime at Hercules. She was awarded the EAS award for achievements in NIR in 1992 and the Delaware Valley Spectroscopist of the Year award in 1999. She has been on editorial boards of journals, and is active in American Chemical Society and Society for Applied Spectroscopy groups. She is currently employed at Alliant Techsystems.

# Chapter 1

## **Introduction to Near-Infrared Spectra**

## 1.1 Molecular Spectra

Molecular spectra result from the periodic motions (or vibrational modes) of atomic nuclei within their respective molecules. These nuclei move together or apart along a straight-line vector; and they rotate, they vibrate, they wag, and they bend relative to their centers of gravity. The vibration and bending of molecules exhibit vibrational spectroscopic activity that may be measured using any number of spectroscopic techniques, including the near-infrared, mid-infrared, far-infrared (terahertz), and Raman spectroscopy. The resultant spectra from these molecular vibrational measurement techniques are highly structured and complex. The process of understanding or characterizing this complexity into the spectra–structure correlations for near-infrared spectra is the purpose of this book.

The energy level in a molecule is described as the sum of the atomic and molecular motions due to translational, rotational, vibrational, and electronic energies. Translational energy has no effect on molecular spectra, whereas the other motions do affect the spectral characteristics. Rotational energy is proportional to the angular velocity of rotation for each molecule. Electronic energy in molecules and their various quantum numbers are described via the Pauli principle and are beyond the scope of this work. We will restrict our discussion to the vibrational energy levels and use the application of what is learned in this model as a basis for our specific structure–correlation characterization of near-infrared (NIR) spectra.

## 1.2 Vibrational Energy Levels

Note that a molecule with  $N$  atoms has three degrees of freedom for motion ( $3N$ ). For all three-dimensional objects, there are three axes of translation ( $x$ ,  $y$ ,  $z$ ) and three axes of rotation (as there are three axes of inertia). If we eliminate these six kinds or types of motion (as they are nonvibrational) we are left with  $3N - 6$  vibrational types of motion. (Note: If the molecule is linear like many polymers there are  $3N - 5$  types of motion.) Each other kind of motion is vibrational in nature and has a specific frequency associated with it. As long as the bonds do not break and the vibrations have motions (amplitudes) of about 10% to 15% of the average distance between atoms, the vibrations are considered harmonic. Any harmonic is considered to be the superposition of two or more vibrations of the molecule and carries the term *normal vibration*.

Frequency of any vibration is not dependent on amplitude. The displacement functions for these normal vibrations are described exactly as a sine-wave function. There are  $3N - 6$  normal vibrations in a molecule and their respective vibrational frequencies are called the fundamental frequencies of the molecule. Symmetry of the molecule is the single factor most important in determining both frequency and amplitude of a molecular vibration. The selection rules discussed later will place a heavy emphasis on symmetry.

## 1.3 Spectral Response and Molecular Concentration

Harmonic vibrations follow a functional description such that the type of vibration determines the frequency at which it absorbs NIR energy. The amplitude of the absorption at any particular wavelength or wavenumber is determined by its absorptivity and the number of molecules encountered within the beam path of the measuring instrument. It is assumed that a change in spectral response is related to a concentration as described by the Bouguer, Lambert, and Beer relationship most often termed *Beer's law*. The Beer's law relationship is described as the absorbance ( $A$ ,  $A_u$ , or signal strength) of an analyte being measured using a spectrophotometer is equivalent to the product of the absorptivity ( $\epsilon$ ) of a specific type of molecular vibration, the concentration ( $c$ ) of the molecules in the measurement beam, and the pathlength ( $l$ ) of the sample holder within the measurement beam. This relationship between measured spectral signal and concentration of a molecule is most often expressed as

$$A = \epsilon cl \quad (1.1)$$

where  $\epsilon$  is the molar absorptivity (referred to as molar extinction coefficient by earlier physicists) in units of  $\text{liter} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ ;  $c$  is the concentration of molecules in the spectrometer beam in units of  $\text{mole} \cdot \text{liter}^{-1}$ ; and  $l$ , the pathlength, is the thickness in units of cm of the measured sample at a specific concentration. The absorptivity for any specific molecule type is calculated by careful measurements of the absorbance of a compound, generally diluted in a suitable organic solvent, and by applying the relationship

$$\epsilon = \frac{A}{cl} \quad (1.2)$$

Note that for transmittance (where  $T = 0.0$  to  $1.0$ ) and percent transmittance (where  $T = 0$  to  $100.0$ ) spectroscopy, a more complete delineation of the relationships between the various terms is contained in an expression such as

$$\begin{aligned} T = \frac{I}{I_0} = 10^{-\epsilon cl} \Rightarrow Abs. = A = -\log_{10} \left( \frac{I}{I_0} \right) \\ = -\log_{10} T = \epsilon cl \end{aligned} \quad (1.3)$$

Here the symbols  $I$  and  $I_0$  represent the attenuated energy detected after sample interaction and the initial energy incident to the sample, respectively. For reflectance (where  $R = 0.0$  to  $1.0$ ) and percent reflectance (where  $R = 0.0$  to  $100.0$ ) spectroscopy the various relationships are expressed as

$$\begin{aligned} R = \frac{I}{I_0} = 10^{-\epsilon cl} \Rightarrow Abs. = A = -\log_{10} \left( \frac{I}{I_0} \right) \\ = -\log_{10} R = \epsilon cl \end{aligned} \quad (1.4)$$

Noting the relationship exists where the change in intensity ( $I$ ) of the transmitted or reflected light from a sample is a function of the change in pathlength ( $l$ ) of the sample as expressed by the absorptivity ( $\epsilon$ ) of a specific analyte (or molecular substance) and its concentration ( $c$ ) by

$$-\frac{\partial I}{\partial l} = \epsilon c I \quad (1.5)$$

Modern spectrophotometers utilize these assumptions for making spectroscopic measurement and generally display spectroscopic data as transmission ( $T$ ), reflection ( $R$ ), and absorbance  $A$  (y-axis or ordinate axis) versus wavelength (nm, microns) or wavenumber ( $\text{cm}^{-1}$ ) (as x-axis or abscissa axis).

## 1.4 Nomenclature of Molecular Vibrations

There are multiple types of molecular vibrations that absorb at unique wavelengths or frequencies of near-infrared energy depending upon the bond type. Several normal (or normal mode) types of molecular vibrations active within the NIR region are illustrated in upcoming figures. Each of these types of vibrations has a unique frequency where absorption occurs. The location of these frequencies and the associated molecular structures (spectra–structure correlations) are the purpose of this book.<sup>1</sup>

## 1.5 Stretching Vibrations

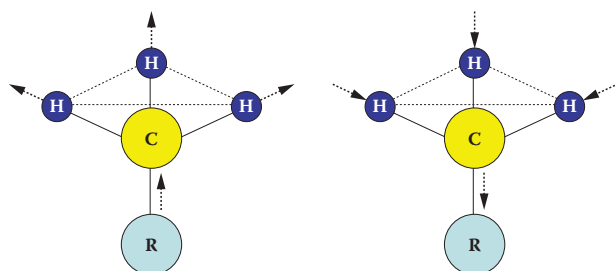
Common nomenclature used in NIR spectroscopy indicates that molecular vibration is a variation of the length of the bond and is indicated with the symbol  $\nu$ . If the group consists of three atoms, instead of two, it can have two types of stretching: asymmetric and symmetric stretching. In order to distinguish the two types of stretching, a subscript is introduced:  $s$  (for the symmetrical stretching) or  $a$  (for the asymmetrical stretching). Figure 1.1 through Figure 1.6 demonstrate stretching vibrational motions in C-H containing molecules.

## 1.6 Bending

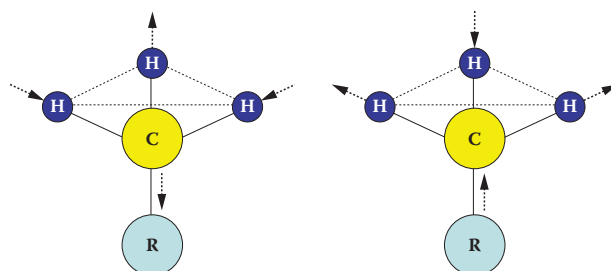
Bending is a variation or change in the angle of a bond occurring on the plane of the bond as indicated with the symbol  $\delta$ . Figure 1.7 through Figure 1.10 show bending molecular motions. If the molecular group consists of four atoms (e.g., one carbon and three hydrogen atoms), instead of 3 (e.g., 1 carbon and 2 hydrogen atoms), they can have two types of bending: symmetrical and asymmetrical bending. Symmetrical bending is indicated by adding the subscript  $s$ , and asymmetrical, the subscript  $a$ . In symmetrical bending (Figure 1.10), the angle 4–1–3, the angle 4–1–2, and the angle 3–1–2 are increased at the same time in the outward movement and are tightened at the same time in the return movement.<sup>2</sup> This is a movement that simulates the opening and the closing of an umbrella. In fact, it is also called *umbrella bending*. In asymmetrical bending, one of the three angles is tightened (in the outward movement), and the other two are increased, and vice versa in the return movement.

## 1.7 Beginning Group Theory for Near-Infrared Spectra

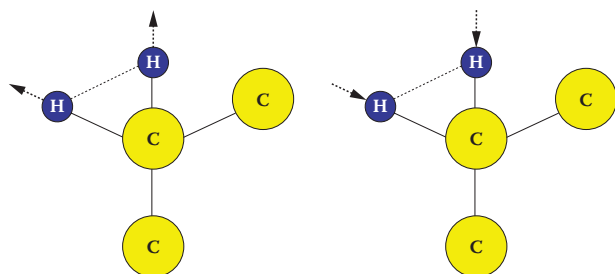
Group theory is used to solve problems in chemistry specifically related to the symmetry properties of a molecule. Near-infrared absorption bands are described using the vibrational energy of the molecules measured. Molecular motion relative to the atomic nuclei is described using the  $x$ ,  $y$ ,  $z$  (Cartesian) coordinate system; for each atom there are 3 degrees of freedom for the motions allowed. If we have  $N$  atoms, then there are 3 times  $N$  degrees of freedom. A more useful way to describe the coordinate space of



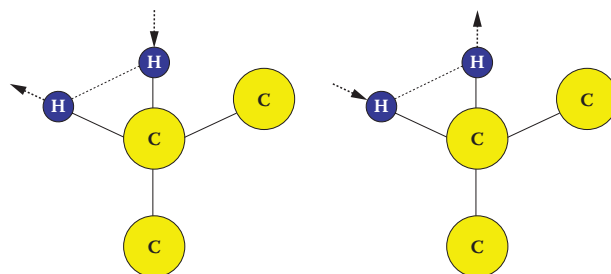
**FIGURE 1.1** Methyl symmetrical stretching of  $\text{CH}_3 \rightarrow \nu_s$ . All atoms are moving toward a similar external direction.



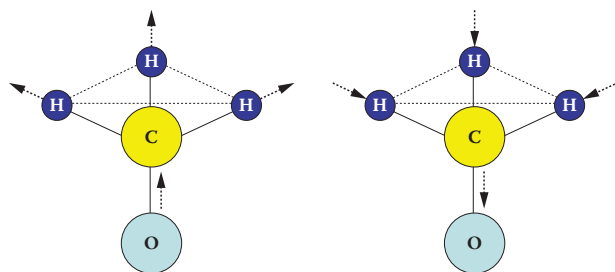
**FIGURE 1.2** Methyl asymmetric stretching of the  $\text{CH}_3 \rightarrow \nu_a$ . Atoms are moving in opposite directions with respect to the carbon.



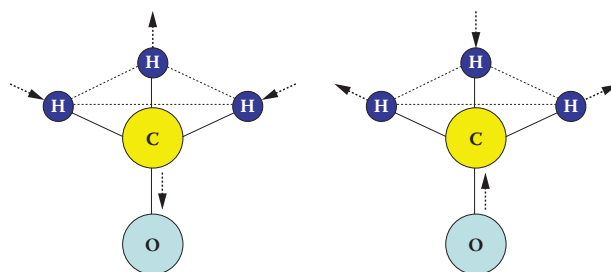
**FIGURE 1.3** Methylene symmetrical stretching of  $\text{CH}_2 \rightarrow \nu_s$ . In this movement the two hydrogen atoms move away from the C at the same time in the outward movement and approach at the same time in the return movement.



**FIGURE 1.4** Methylene asymmetric stretching of the  $\text{CH}_2 \rightarrow \nu_a$ . In this movement, while one hydrogen is moving away from the carbon atom, the other is approaching.



**FIGURE 1.5** Symmetrical stretching of  $\text{O-C-H} \rightarrow \nu_s$ . In this movement, the two hydrogen atoms go away from the C at the same time in the outward movement and approach at the same time in the return movement. The oxygen atom is moving in a likewise external direction as the hydrogen atoms with respect to the carbon atom.

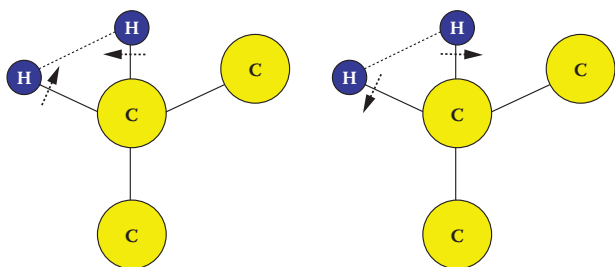


**FIGURE 1.6** Asymmetric stretching of  $\text{O-C-H} \rightarrow \nu_a$ . In this movement, while one hydrogen moves away from the carbon atom, the other two approach. In the second type of asymmetrical motion, two hydrogen atoms move away from the carbon while the other moves toward the carbon atom.

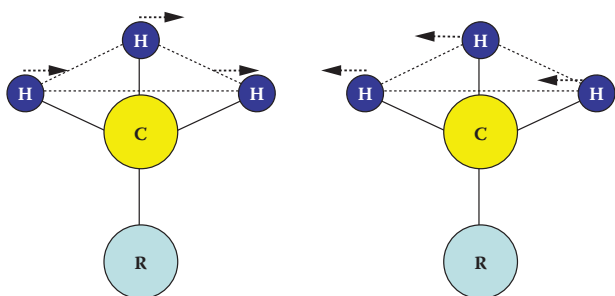
molecules is by the use of group theory. Group theory requires some basic mathematics and an understanding of the modern theories of the three-dimensional shape of molecules. Symmetry can be surmised to have an affect on the energy levels of a molecule simply by examining its spectrum. This applies to infrared, Raman, far-infrared (terahertz), near-infrared, and  $^1\text{H}$ -NMR spectra.

It is not very satisfying nor quantitative to argue that the hydrogen atoms in a symmetrical molecule are all in the same “chemical” or atomic/molecular environment and thus should all “look” the same spectrally. This is certainly true but neither precise nor informative. The rules of symmetry can be precisely and mathematically described, and it is the object of group theory to be useful for prediction





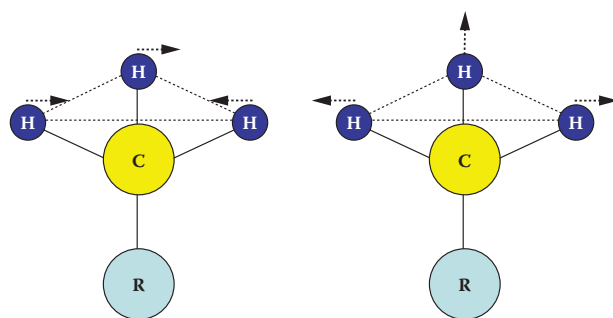
**FIGURE 1.7** Methylene bending of  $\text{CH}_2 \rightarrow \delta$ . The two methylene hydrogen atoms move toward each other or away from each other simultaneously.



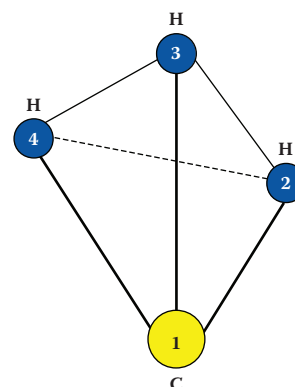
**FIGURE 1.9** Methyl asymmetric bending of  $\text{CH} \rightarrow \delta_a$ .  
of spectroscopic complexity based upon energy levels. The first concepts and terms that will help to introduce group theory include rotational axes, reflection planes, inversion centers, improper rotational axes, and point groups. The symmetry of a molecule can be described in mathematical notation in terms of its symmetry operations. Excellent references describing group theory include Norman et al.<sup>2</sup> and Walton.<sup>3</sup>

## 1.8 Rotational Axes

Operations of rotation about an axis represented by a central atom in a molecule are important concepts in group theory. A completely symmetrical molecule can be rotated 180 degrees about its central axis and produce a molecule that is “indistinguishable” from its original; a 360-degree rotation produces an “identical” molecule. Note this indicates that labeled molecules would be in different positions relative to a fixed observer for the 180-degree rotation and be in identical positions for two successive 180-degree rotations. The order of these rotational axes



**FIGURE 1.8** Methyl symmetrical bending of  $\text{CH}_3 \rightarrow \delta_s$ .



**FIGURE 1.10** Internal umbrella (symmetrical) bending motion of tetrahedron  $\text{CH}_3$ .

is represented mathematically by the ratio of  $360/r$ , where  $r$  is the number of degrees of rotation around an axis that produces an indistinguishable molecule. For example, an  $\text{Sp}^3$  molecule requires a 120-degree rotation along the long axis of the molecule and is thus 3rd order. A molecule like cyclohexane or benzene when rotated around its principal axis (the axis perpendicular to the plane of the molecule) would require a 60-degree rotation and therefore have an order of 6.

## 1.9 Reflection Planes

The concept of reflection planes refers to symmetry assessed using the mirror image approach. If an imaginary double-sided mirror is used to bisect the molecule along various planes, then the reflection from each side of the mirror is used to reconstruct the other side of the molecule. So once this mental reconstruction or visualization of the molecule is completed, a symmetrical molecule will be indistinguishable from the original when using this method.

## 1.10 Inversion Centers

Inversion centers, referred to as *i*, are another instrument for demonstrating the symmetry of a molecule. Unlike the rotational and reflection methods for which a molecule may have many axes or planes, respectively, there is only one inversion center per molecule. For this exercise to test symmetry imagine that each molecule has a center of mass with bonds at opposite ends of the molecule. If the atoms at the ends of these bonds are inverted or switched with one another, does the inverted form of the molecule remain indistinguishable as compared to the original? If so, the molecule is symmetrical.

## 1.11 Improper Rotational Axes

Improper rotation is a symmetry operation needed on a molecule where one of the atoms lies along the rotation axis and cannot be transformed into the position of other atoms on the molecule simply by rotation or reflection methods. In this case the improper rotation axis must be used to bring this atom into the position of other atoms so it can be transformed (by rotation or reflection) into the position of the other atoms. Methane can be used as an example molecule. See Figure 1.11(d).

## 1.12 Point Groups

The point group system is a formal nomenclature method for designating symmetry operations. Point indicates the single point in space that each symmetry operation passes through; this can be either a central atom within a molecule or a center of mass for a molecule without a central atom. The term *group* indicates a group of symmetry operations around the designated point. There is a set of symmetry rules that are used to classify a molecule by point groups.

## 1.13 Defining a Group Using Matrix Operations

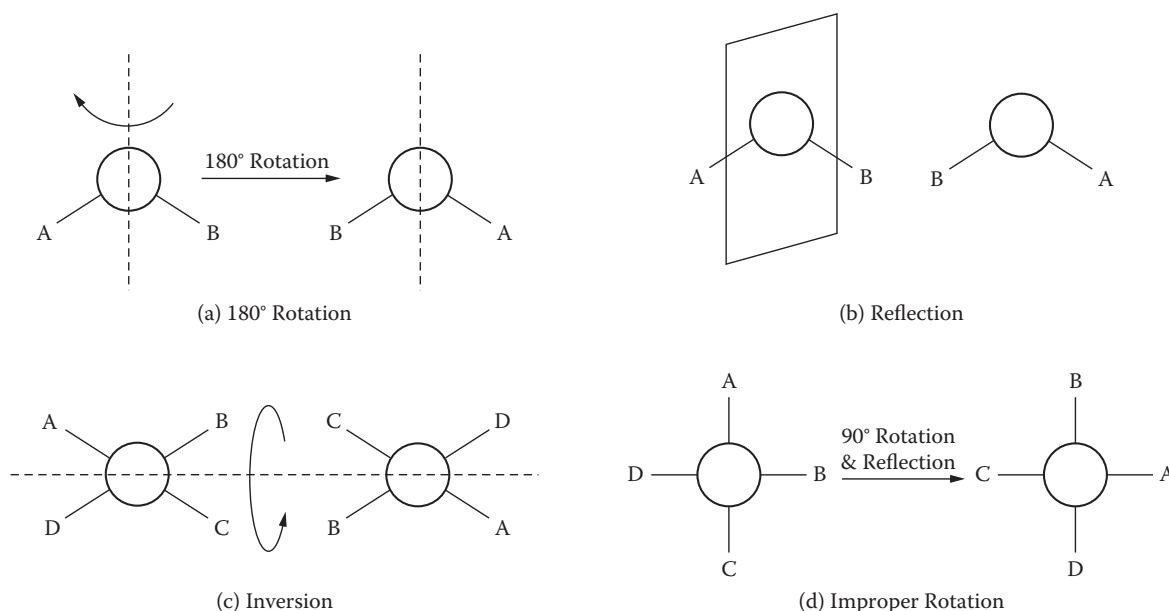
A group for this discussion may be described as a formation of atoms interacting as a molecular association and having a common set of rules whereby motion is allowed under specific prescribed conditions. There are verbal descriptive definitions for such groups, but mathematics provides a precise description. The mathematics used

includes the use of basic matrix algebra. Some definitions are useful. An *identity* operation is the result of a combination of events; a combination of events follows *associative properties* (in a mathematical sense), and there is an *inverse* operation for all events. So to give mathematical definitions for these terms using matrix notation is extremely useful. Matrix multiplication is also used due to its importance in describing group interactions.

All molecules have symmetry elements in their structures. These structures have only certain potential motions allowed around any particular plane or rotational axis. For example with crystal structures there are a limit of 32 possible combinations of symmetry elements (or motions) allowed. These individual allowed motions are also termed *point groups*.<sup>2</sup> There are 32 groups plus some additional groups that have specific axes of symmetry for most molecules. Each of the groups has specific names and prescribed motions. These possible rotational motions are represented or expressed in matrix notation and described by using the standard matrix operations shown below. The reader is referred to Chapters 3 and 14 of Colthup, Daly, and Wiberly's classic infrared text for a thorough explanation.<sup>2</sup> Walton providing a working tutorial on the subject.<sup>3</sup> Walton also summarizes group theory with eight points, noting that symmetry elements are comprised of rotational axes, reflection planes, inversion centers, and improper rotation axes as illustrated by the characters in Figure 1.11. More details and descriptions of these molecular properties are to be found in references 2 and 3.

## 1.14 Practical Aspects for Spectral Measurements

A variety of sample presentation methods are available to the analytical scientist. These include transmission (straight and diffuse), reflection (specular and diffuse), transfection (reflection and transmission), and interaction (a combination of reflection and transmission). Pathlength selection for optimum near-infrared measurements involves the following: For the shortwave near-infrared (SW-NIR) region of 12500 to 9091  $\text{cm}^{-1}$  (800–1100 nm), pathlengths ranging from 5–10 cm are typically used. For longwave near infrared (LW-NIR) or 9091 to 4000  $\text{cm}^{-1}$  (1100–2500 nm), common pathlengths for hydrocarbons include 0.1–2 cm or 1 mm to 20 mm.



**FIGURE 1.11** The symmetry operations of a molecule.

The sample presentation geometries most often used in NIR measurements are given in Table 1.1. For this table, the abbreviations used designate transmission (T), diffuse transmission (DT), and diffuse reflection (DR). Transmission and diffuse transmission are the identical sample presentation geometry, but the sample for DT is a series of particles allowing light to penetrate without significant backscatter. DR is used for samples of infinite optical thickness that will not transmit light if T or DT is used. The ideal surface for DR is a Lambertian or isotropic surface where light is reflected diffusely or evenly throughout a hemisphere above the surface.

Samples exhibit different optical characteristics that must be considered to optimize spectroscopic measurement. Standard clear samples or solutions are measured using transmission spectroscopy. Highly colored samples

are generally measured using transmission spectroscopy unless the optical density exceeds the linear range of the measuring instrument. At this point either dilution or reducing the pathlength is preferred.

Fine scattering particulates of 5 to 25 times the measuring wavelength are measured using diffuse transmission or diffuse reflection methods. The scattering produced by some of the reflected light creates a pseudo-pathlength effect. This effect is compensated for by using scatter correction data processing methods for quantitative measurements, sieving the particles, or grinding to improved particle size uniformity.

Large scattering particulates on the order of 100 times the measuring wavelength in diameter present a challenge for measurements as the particles intercept the optical path at random intervals. Signal averaging can be employed

**Table 1.1** Sample Presentation Methods for Polymers and Rubbers

| Sample Type   | Sample Presentation | Comments  |
|---|---------------------|---|
| Liquids (lower viscosity)   | T and DT            | Maintain instrument within linear measurement range, that is generally less than 1.5 Au |
| Slurries (high viscosity)   | T and DT            | Maintain instrument within linear measurement range, that is generally less than 1.5 Au |
| Solids and smaller particles  | DR                  | For DR use infinite optical thickness   |
| Webs  | DR and DT           | For DR use infinite optical thickness   |
| Pellets (large particles)   | DR and DT           | For DR use infinite optical thickness   |
| <i>Note:</i> Transmission, T; diffuse transmission, DT; diffuse reflection, DR. |                     |   |

**Table 1.2 Relative Band Intensities: MIR versus NIR for C-H Stretch**

| Band                       | Wavenumber (Wavelength) Region            | Relative Intensity | Recommended Sample Cell Pathlength (for Liquid Hydrocarbons) |
|----------------------------|---|--------------------|--|
| Fundamental ( $\nu$ )      | 2959–2849 $\text{cm}^{-1}$ (3380–3510 nm) | 1                  | 0.1–4 mm   |
| First overtone ( $2\nu$ )  | 5917–5698 $\text{cm}^{-1}$ (1690–1755 nm) | 0.01               | 0.1–2 cm   |
| Second overtone ( $3\nu$ ) | 8873–8547 $\text{cm}^{-1}$ (1127–1170 nm) | 0.001              | 0.5–5 cm   |
| Third overtone ( $4\nu$ )  | 11834–11390 $\text{cm}^{-1}$ (845–878 nm) | 0.0001             | 5–10 cm  |
| Fourth overtone ( $5\nu$ ) | 14493–12987 $\text{cm}^{-1}$ (690–770 nm) | 0.00005            | 10–20 cm   |

to compensate for random signal fluctuations. Reflection spectroscopy can be used to measure the size, velocity, and concentration of scattering particulates within a flowing stream.

Very high absorptivity (optically dense) materials with absorbances above 4 to 6 Au are difficult to measure accurately without the use of high precision photometric instruments, such as high performance Fourier transform interferometers or double monochromator systems. Such samples should be measured with instruments having stray light specifications below 0.0001 percent T. Measurements of such samples can be made using higher numbers of repetitive scans, in the case of interferometric measurements, or by extremely slow scanning speeds, when using monochromator instruments.

Mid-infrared fundamental bands have high absorptivity values, however, their corresponding near-infrared combination and overtone bands have the advantage of lower absorption and therefore are more convenient for in situ or high-moisture sample measurements. The repetitive information provided by the various overtone and combination bands in the near infrared provides an opportunity for selection of the appropriate pathlength

for measurement. Table 1.2 shows the relative absorption band intensities for each particular band as well as general spectral regions for fundamental through fourth overtone C-H stretching absorptions.

### 1.15 Types of Near-Infrared Absorption Bands

Infrared energy is the electromagnetic energy of molecular vibration. The energy band is defined for convenience as the near-infrared covering 12821 to 4000  $\text{cm}^{-1}$  (780 to 2500 nm); the infrared (or mid-infrared) as 4000 to 400  $\text{cm}^{-1}$  (2500 to 25000 nm); and the far infrared (or terahertz) from 400 to 10  $\text{cm}^{-1}$  (25000 to 1000000 nm). Table 1.3 illustrates the region of the EMR (electromagnetic radiation) spectrum referred to as the NIR region. The table shows the molecular interactions associated with the energy frequencies (or corresponding wavelengths) of the various regions.

Specific molecular bonds most active in the NIR are listed next, with X-H bonds being the more active and intense. The X-H bonds are most active since the masses of carbon (C) and hydrogen (H) differ significantly, and

**Table 1.3 Spectroscopic Regions of Interest for Chemical Analysis**

| Region                          | Wavenumbers (Wavelength)  | Characteristic Measured  |
|---------------------------------|---|--|
| Ultraviolet                     | 52632–27778 $\text{cm}^{-1}$ (190–360 nm)   | Electronic transitions: delocalized $\pi$ electrons  |
| Visible                         | 27778–12821 $\text{cm}^{-1}$ (360–780 nm)   | Electronic transitions: color measurements   |
| Near infrared (NIR)             | 14493–3333 $\text{cm}^{-1}$ (690–3000 nm) or 12821–4000 $\text{cm}^{-1}$ (780–2500 nm)* | Overtone and combination bands of fundamental molecular vibrations, especially stretching and bending (some deformation as well) |
| Infrared (IR)                   | 4000–400 $\text{cm}^{-1}$ (2500–25000 nm)   | Fundamental molecular vibrations: stretching, bending, wagging, scissoring   |
| Far infrared (FIR or terahertz) | 400–10 $\text{cm}^{-1}$ ( $2.5 \times 10^4$ to $10^6$ nm)                               | Molecular rotation   |

\* Official ASTM International definition.

**Table 1.4** Equivalent Wavelength, Wavenumber, and Frequency Values for the Visible and Near-Infrared Spectral Regions

| Region                 | Wavelength (cm)                              | Wavelength ( $\mu\text{m}$ ) | Wavelength (nm) | Wavenumber ( $\text{cm}^{-1}$ ) | Frequency (Hz)                                   |
|------------------------|--|------------------------------|-----------------|---------------------------------|--|
| Visible                | $3.5 \times 10^{-5}$ to $7.8 \times 10^{-5}$ | 0.35 to 0.78                 | 350 to 780      | 28571 to 12821                  | $8.563 \times 10^{14}$ to $3.842 \times 10^{14}$ |
| Extended near-infrared | $7.8 \times 10^{-5}$ to $3.0 \times 10^{-4}$ | 0.78 to 3.0                  | 780 to 3000     | 12821 to 3333                   | $3.842 \times 10^{14}$ to $9.989 \times 10^{13}$ |

have harmonics of their stretching and bending vibrations that absorb energy or vibrate at a higher frequency than the fundamental bands.

C=O from aldehydes  
 C=O from amides  
 C=O from carboxylic acids  
 C=O from esters  
 C=O from ketones  
 C-H from aldehydes  
 C-H from alkanes  
 C-H from alkenes  
 C-H from alkynes  
 C-H from aromatic compounds  
 N-H from amides  
 N-H from amines  
 O-H from alcohols (no hydrogen bonding)  
 O-H from alcohols (with hydrogen bonding)  
 O-H from carboxylic acids

## 1.16 Properties of Infrared-Near-Infrared Energy

Light has both particle and wave properties. Quantum theory tells us that the energy of a light “particle” or photon  $E_p$  is given by

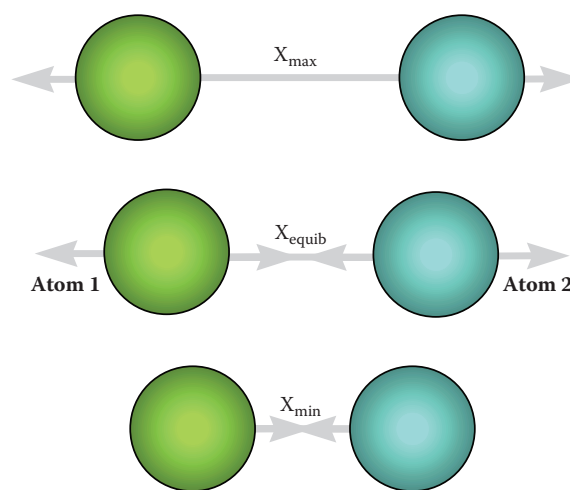
$$E_p = h\nu \quad (1.6)$$

where  $h$  is Planck’s constant (or  $6.6256 \times 10^{-27}$  erg/sec) and  $\nu$  is the frequency of light, also known as hertz (Hz) or the number of vibrations per second in units of  $\text{sec}^{-1}$ . Thus the energy for any specific photon can be quantified, and it is this energy that interacts with the vibrating bonds within *near-infrared active molecules*. The subsequent values for wavelength, wavenumber, and frequency for both the visible and the extended near-infrared regions are shown in Table 1.4.

## 1.17 Normal Mode Theory (The Ideal Harmonic Oscillator)

Light from a spectrophotometer is directed to strike a matrix consisting of one or more types of molecules. If the molecules do not interact with the light, then the light passes through the matrix with no interaction whatsoever. If molecules interact with the light in a very specific way (i.e., molecular absorption) we refer to them as *active* or *infrared active*. For NIR energy, the overtones of X-H bonds, that is, N-H, C-H, and O-H, stretching and bending are of the greatest interest. Infrared active molecules can be seen as consisting of mechanical models with vibrating dipoles. Each dipole model vibrates with a specific frequency and amplitude as shown using a simple model (Figure 1.12).

Note that the term *frequency* refers to the number of vibrations per unit of time, designated by the Greek letter  $\nu$  (nu) and generally specified in units of  $\text{sec}^{-1}$  or hertz (Hz). *Amplitude* is defined by the interatomic distance covered



**FIGURE 1.12** Model of infrared active molecule as a vibrating dipole between two atoms. (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. 1996, 31(3), 251–320. With permission.)



at the extremes of the vibrating dipole and is dependent upon the amount of energy absorbed by the infrared (or near-infrared) active bond. When incoming photons from a spectrophotometer source lamp (after they have passed through the monochromator or interferometer optics) strike different molecules in a sample, two direct results may occur: (1) the disturbing energy does not match one or more of the natural vibrational frequencies of the molecule; or (2) the disturbing frequency does match one or more of the vibrational frequencies of the molecule. When there is a match between the disturbing frequency of the illumination energy and the natural vibrational frequency of a molecule in the sample, the molecule absorbs this energy, which in turn increases the vibrational amplitude (oscillation distance) of the absorbing dipoles. However, regardless of the increase in amplitude, the frequency of the absorbing vibration remains constant.

Another name for the dipole model from Figure 1.12 is an *ideal harmonic oscillator*. The frequency at which the dipole (or ideal harmonic oscillator) vibrates (stretches or bends) is dependent upon the bond strength and the masses of the atoms bonded together. When the harmonic oscillator (HO) vibrates, the vibrational energy is continuously changing from kinetic to potential and back again. The total energy in the bond is proportional to the frequency of the vibration. The use of Hooke's law (in our case referring to the elasticity properties of the HO) is applied to illustrate the properties of the two atoms with a well-behaved spring-like bond motion between them. The natural frequency of vibration for a bond (or any two masses connected by a spring) is given by the well-known relationship

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\left(\frac{1}{m_1} + \frac{1}{m_2}\right)}} \quad (1.7)$$

where  $k$  is a force constant that varies from one bond to another,  $m_1$  is the mass of atom 1, and  $m_2$  is the mass of atom 2. Note: As a first approximation the force constant ( $k$ ) for single bonds is half times that of a double bond and one-third that of a triple bond. Also note that as the mass of the atoms increases the frequency of the vibration decreases.

Group theory can be used to represent the associations or bonds between the atoms of molecules into one-dimensional simple springs or simple harmonic oscillators.

Normal mode theory, using the simple harmonic oscillator model, is able to predict with relative accuracy the energy or frequency of fundamental absorption bands, such as symmetric and asymmetric stretching, scissoring, bending, and wagging. However, for overtone band positions, normal mode theory does not predict band positions exactly since bonds are not true harmonic oscillators. The effects of quantum mechanics on a simple HO indicate that the bond interaction between two atoms is not as simplistic as a description of two masses connected by a spring. This is no surprise since quantum mechanical evidence has shown that vibrational energy between atoms in a molecule is quantized into discrete energy levels. When the conditions are right, vibrational energy in a molecule "jumps" from one energy level to another. The discrete vibrational energy levels for any molecule,  $E_{VIB}$ , are given by

$$E_{VIB} = h\nu \left( \nu + \frac{1}{2} \right) \quad (1.8)$$

where  $h$  is Planck's constant,  $\nu$  is the vibrational frequency of the bond, and  $\nu$  is the vibrational quantum number (which can only have the integer values of 0, 1, 2, 3, 4, and so on).

## 1.18 The Anharmonic Oscillator

The *anharmonic oscillator* model has been used to predict the relative positions of harmonics or overtone vibrations, especially when the higher harmonics or overtones ( $\nu$ ) are concerned (i.e.,  $\nu = 2, 3, 4, 5, 6$ , etc.). The anharmonic oscillator model is used to describe the higher energy states or overtones of molecular vibrations. In its simplified expression it estimates the vibrational energy states of the molecular vibrational harmonic bands, providing more realistic calculations of the frequency positions of the allowed overtone transitions. The energy levels for these overtones are not found as the product of exact integer multiples and the fundamental absorption frequencies. In fact, the following expression defines the relationship between wavenumber (for a given bond energy) and the vibrational frequency of the harmonics for a fundamental vibration. This relationship is calculated from the Schrödinger equation to yield Equation 1.9.

$$\nu = \left( \frac{E_{VIB}}{hc} \right) = \nu_1 \nu - x_1 \nu_1 (\nu + \nu^2) \quad (1.9)$$

where  $\nu$  is an integer overtone number, that is, 0, 1, 2, 3, ...,  $n$ ; and  $x_1\nu_1$  is the unique anharmonicity constant for each bond.

Calculations of band positions using Equation 1.9 will more closely approximate observed band positions than those calculated from the ideal harmonic oscillator expression found in Equation 1.7. As a rule of thumb, the first overtone ( $2\nu$ ) for a fundamental can be calculated as 1% shift due to anharmonicity or  $x_1 = (0.01)$ . Thus the expression using wavenumbers is

$$\nu = \nu_1\nu - \nu_1(0.01) \cdot (\nu + \nu^2) \quad (1.10)$$

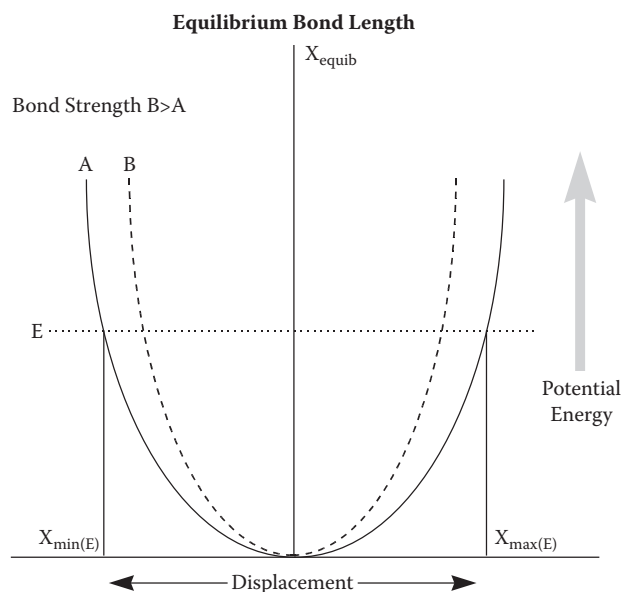
To illustrate the occurrence of the free O-H first overtone absorption, using a fundamental absorption occurring at approximately  $3625\text{ cm}^{-1}$ , the first overtone (in wavenumbers) for free O-H stretching ( $2\nu$ ) should occur at

$$\begin{aligned} \nu &= (3625 \cdot 2) - 3625(0.01) \cdot (2 + 2^2) = 7033\text{ cm}^{-1} \\ &\text{or } 1422\text{ nm} \end{aligned} \quad (1.11)$$

Thus, if this expression holds true one would expect the free O-H first overtone to occur somewhere near  $7033\text{ cm}^{-1}$  or  $1422\text{ nm}$  using a simple harmonic oscillator model. To convert to wavelength (nanometers), use  $10^7 \div \nu$  (in  $\text{cm}^{-1}$ ). Calculations for wavenumber positions for the first overtone ( $2\nu$ ), second overtone ( $3\nu$ ), and third overtone ( $4\nu$ ) can be estimated with the assumption of a 1% to 5% frequency shift due to anharmonicity, as one increases the transition (overtone) number ( $\nu$ ).

Molecules that absorb NIR energy vibrate primarily in two fundamental modes: (1) stretching and (2) bending. Stretching is defined as a continuous change in the interatomic distance along the axis between two atoms, and bending is defined as a change in the bond angle between two atoms. Figure 1.13 illustrates the potential energy change caused by the minimum and maximum displacement of atoms for a stretching vibration within infrared active molecules.

Note that near-infrared ( $12821\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ ;  $780$  to  $2500\text{ nm}$ ) spectral features arise from the molecular absorptions of the overtones and combination bands from fundamental vibrational bands located in the mid-infrared region. For fundamental vibrations there exists a series of overtones with decreasing intensity as the transition number (overtone or  $\nu$ ) increases. Combination bands arise



**FIGURE 1.13** Potential energy curve showing minimum and maximum amplitude for the harmonic oscillator model of a molecular stretching vibration as a continuum. (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. 1996, 31(3), 251–320. With permission.)

as the summation of fundamental bands, their intensity decreasing with an increase in the summation frequency. Most near-infrared absorptions result from the harmonics and overtones of X-H fundamental stretching and bending vibrational modes. Other functional groups relative to near-infrared spectroscopy can include hydrogen bonding, carbonyl carbon to oxygen stretch, carbon to nitrogen stretch, carbon to carbon stretch, and metal halides.

Molecular vibrations in the near-infrared regions consist of stretching and bending combination and overtone bands. Stretching vibrations occur at higher frequencies (lower wavelengths) than bending vibrations. Stretching vibrations are either symmetric or asymmetric; bending vibrations are either in plane or out of plane. In-plane bending consists of scissoring and rocking; out-of-plane bending consists of wagging and twisting. From highest frequency to lowest, the vibrational modes occur as stretching, in-plane bending (scissoring), out-of-plane bending (wagging), twisting, and rocking. The most often observed bands in the near infrared include the combination bands and first, second, or third overtones of O-H, N-H, and C-H fundamental vibrations.

Fundamental and overtone absorptions arise when molecules are excited from the ground state to a higher energy excited state. Fundamental vibrations will change in amplitude when absorbing energy of the same frequency from an outside source strikes the vibrating bond(s).

Variations in hydrogen bonding manifest themselves as changes in the force constants of the X-H bonds. Generally bands will shift in frequency and broaden due to the formation of hydrogen bonding. Since combination bands result as the summation of two or more fundamental vibrations, and overtones occur as the result of the multiples of fundamental vibrations, frequency shifts related to hydrogen bonding have a greater relative effect on combination and overtone bands than on their corresponding fundamentals. The reason for this is that harmonics have weaker bond energies relative to the hydrogen bonding and have greater anharmonicity. This feature of the near-infrared region alerts one to the importance of the relative hydrogen bonding effects brought about by solvent and temperature variations.

Precise band assignments are difficult in the near-infrared region due to the fact that a single band may be attributable to several possible combinations of fundamental and overtone vibrations all severely overlapped. The influence of hydrogen bonding results in band shifts to lower frequencies (higher wavelengths); a decrease in hydrogen bonding due to dilution and higher temperatures results in band shifts to higher frequencies (lower wavelengths). Band shifts of the magnitude of 10 to 100  $\text{cm}^{-1}$ , corresponding to a few nanometers to 50 nm may be observed. The substantial effect of hydrogen bonding should be kept in the forefront of thought when composing calibration sample sets and experimental designs for near-infrared experiments.

Near-infrared spectra contain information relating to differences in bond strengths, chemical species, electronegativity, and hydrogen bonding. For solid samples, information with respect to scattering, diffuse reflection, specular reflection, surface gloss, refractive index, and polarization of reflected light are all superimposed on the near-infrared vibrational information. Aspects related to hydrogen bonding and hydronium ion concentration are also included within the spectral shapes.

Light can interact with the sample as reflection, refraction, absorption, scattering, diffraction, and transmission. Signal losses from the sample can occur as specular

reflection, internal scattering, refraction, complete absorption, transmission loss during reflectance measurements, and trapping losses. Spectral artifacts can also arise as offset or multiplicative errors due to coloration of the sample, variable particle sizes and resultant variability in apparent pathlength, refractive index changes in clear liquids relative to temperature changes, and pathlength differences due to temperature induced density changes.

During measurement of a sample, the light energy entering the sample will be attenuated to some extent; the light entering the sample is able to interact with the sample emerging as attenuated transmitted or reflected light. The frequency and quantity of light absorbed yields information regarding both the physical and compositional information of the sample. For reflection spectra the diffuse and specular energy fractions are superimposed. The intensity of reflected energy is a function of multiple factors, including the angles of incidence and observation; the sample packing density, crystalline structure, refractive index, particle size and distribution, absorptive and scattering qualities.

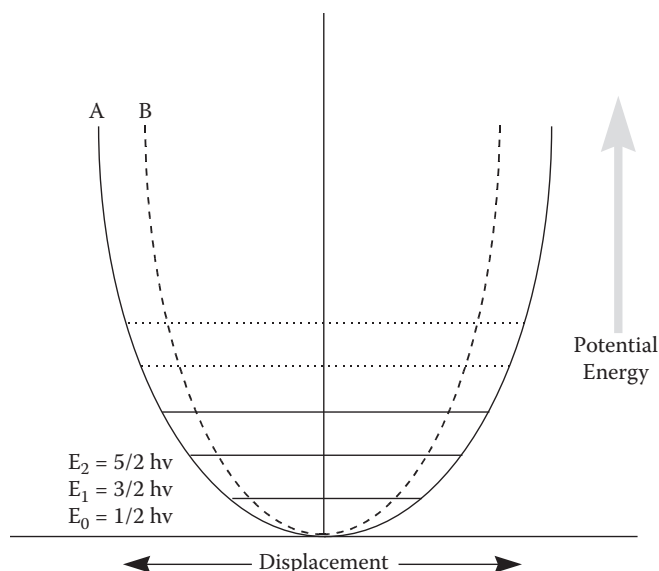
The types of vibrations found in near-infrared and infrared spectroscopy are designated by the Greek lower case nu ( $\nu$ ) with a subscript designating whether the vibration is symmetric (*s*) or asymmetric (*a*); bending vibrational modes are designated using the Greek lower case delta ( $\delta$ ). Combination bands resulting from the sum of stretching and bending modes are designated as  $\nu + \delta$ ; and harmonics are designated as  $\nu\nu$ , where  $\nu$  is an integer number as 2 (first overtone), 3 (second overtone), ...,  $\nu$  ( $\nu - 1$  overtone), and  $\nu$  is the frequency of the fundamental stretching vibration for a specific functionality.

### 1.19 Illustration of the Harmonic Oscillator or Normal Mode

The classical harmonic oscillator model or normal mode is often illustrated using a potential energy curve (Figure 1.14). The larger the mass, the lower the frequency of the molecular vibration, yet the potential energy curve does not change. The relationship for a simple diatomic molecule model is

$$\text{Frequency} = \nu(\text{Gr.Nu}) = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (1.12)$$





**FIGURE 1.14** Illustration of the discrete quanta potential energy curves ( $E_0$ ,  $E_1$ ,  $E_2$ , etc.) for both strongly and weakly bonded dipoles as  $E_n = \left(n + \frac{1}{2}\right)h\nu$ . (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. 1996, 31(3), 251–320. With permission.)

where  $k$  is the force constant for the bond holding the two atoms together, and  $m$  is the reduced mass from the individual atoms, as described in Eq. 1.12.

For any bond there is a limit to the amplitude of motion away from and toward the opposing atom ( $X_{\max}$  and  $X_{\min}$ , respectively). The potential energy increases at either extreme, that is, either the minimum or maximum distance between atoms. The total potential energy ( $E_t$ ) for a bond following the harmonic oscillator model is given by  $E_t = \frac{1}{2}k \cdot x^2$ , where  $k$  is the force constant for the bond holding the two atoms together, and  $x$  is the change in displacement from the center of equilibrium. For any specific bond there is a limit to the total energy and maximum displacement of the atoms (or dipoles). Quantum mechanical theory is used to more closely describe the behavior of these atoms connected by bonds with varying force constants. Using quantum theory it is possible to describe a mathematical relationship for the behavior of two oscillating atoms as following not a continuous change in potential energy states for the vibrating system but actually a set of discrete energy levels ( $E_n$ ) given by  $E_n = \left(n + \frac{1}{2}\right)h\nu$ , where  $n$  is the oscillating dipole quantum number for

discrete potential energy levels, that is, 0, 1, 2, 3, ...,  $n$ . The potential energy curve better describing the behavior of oscillating dipoles is given in Figure 1.14.

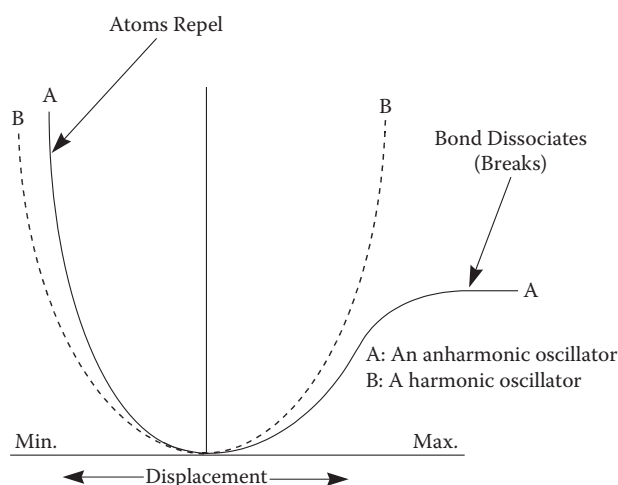
## 1.20 The Selection Rule

The selection rule states that in the quantum mechanical model a molecule may only absorb (or emit) light of an energy equal to the spacing between two levels. For the harmonic oscillator (dipole involving two atoms) the transitions can only occur from one level to the next higher (or lower) transition level.

The infrared spectrum for any molecule will exhibit a band corresponding to the frequency of the energy at which light can absorb, namely,  $E_0$ ,  $E_1$ ,  $E_3$ , and so forth. Figure 1.14 illustrates the discrete quanta potential energy curves for both strongly and weakly bonded dipoles. The energy levels are not equally spaced for the harmonic oscillator as shown below. Note that the figure illustrates the energy levels for the fundamental vibrations (or oscillations) only. In addition to the fundamentals, the overtone bands also occur at less than 2 times, 3 times, and 4 times the frequency of the fundamental vibrations, and at much less intensity. Further discussions in this book will describe the factors involving the infrared and near infrared spectroscopic activity of molecules.

## 1.21 Illustration of the Anharmonic Oscillator

As previously described, the model of the anharmonic oscillator more closely follows the actual condition for molecular absorption than that of the harmonic oscillator. Figure 1.15 illustrates the differences between the ideal harmonic oscillator case, which has been discussed in detail for this chapter, versus the anharmonic oscillator model (better representing the actual condition of molecules). Unlike the ideal model illustrated by the harmonic oscillator expression, the anharmonic oscillator involves considerations such that when two atoms are in close proximity (minimum distance) they repel each other; when too large a distance separates two atoms, the bond breaks. The anharmonic oscillator potential energy curve is more useful to predict behavior of real molecules.



**FIGURE 1.15** Illustration for the differences in potential energy curves between the ideal harmonic oscillator model and the harmonic oscillator model (better representing the actual condition of molecules). (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. **1996**, 31(3), 251–320. With permission.)

## 1.22 Local Mode Theory (Morse Oscillator)

Local mode theory is used to formulate an understanding of the higher-order NIR overtones for X-H groups, for example,  $\nu = 2, 3, 4, 5$ . In this theory molecules can be treated as a set of equivalent diatomic oscillators and anharmonicity dominates over interbond coupling when the energy levels for bond vibrations move to higher energies. The vibrations are coupled for complex molecules and become uncoupled when the spectra are of simpler molecular structure.

The local mode model is used to describe the frequency ( $\nu$ ) for X-H overtones or transitions using the Morse oscillator model (Equation 1.14). It is a theoretical and practical improvement over the normal mode descriptive model. It has become more prominent in estimations of overtone transition absorption frequencies and is based on early and continued work by B. R. Henry (University of Guelph)<sup>4,5</sup> and others. It differs from Equation 1.9 to Equation 1.11, which demonstrate the anharmonic oscillator model with its rule of thumb example shown for estimating the first overtone free O-H stretching ( $2\nu$ ) band position. Equation 1.14 and Equation 1.15 use the Morse oscillator model for estimating this same band position and are illustrated for comparison.

Anharmonic oscillator model:

$$\nu = \left( \frac{E_{\text{VIB}}}{hc} \right) = \nu_1 \nu - x_{1A} \nu_1 (\nu + \nu^2) \quad (1.13)$$

Morse oscillator model:

$$\nu = \left( \frac{E_{\text{VIB}}}{hc} \right) = \nu_1 \left( \nu + \frac{1}{2} \right) - x_{1M} \nu_1 \left( \nu + \frac{1}{2} \right)^2 \quad (1.14)$$

where  $\nu$  is an integer harmonic number, that is, 0, 1, 2, 3, ...,  $n$ ; and  $x_{1X}\nu_1$  is the unique constant for each bond.

Calculations of band positions using the Morse oscillator model for the first overtone free O-H stretching ( $2\nu$ ) as Equation 1.14 and Equation 1.15 will even more closely approximate observed band positions than those calculated from the ideal harmonic oscillator expression found in Equation 1.7 or the anharmonicity model as Equations 1.9–1.11.

To illustrate the Morse oscillator model we refer to Equation 1.14 for the occurrence of the free O-H first overtone ( $\nu = 2$ ) absorption in water, near freezing temperature. Note: For this example, the computation is for  $\nu = 2 \leftarrow \nu = 0$ ; and  $x_{1M} = 0.0963$ ;  $x_{1M}\nu_1 = 349.09$ . Then using a fundamental O-H absorption occurring at approximately  $3625 \text{ cm}^{-1}$ , the first overtone (in wavenumbers) for free O-H stretching should occur at  $1452 \text{ nm}$ , a precise calculated location.

$$\nu = (3625 \cdot 2.5) - 3625(0.0963) \cdot (2.5^2) = 6880 \text{ cm}^{-1} \quad \text{or } 1452 \text{ nm} \quad (1.15)$$

## 1.23 Interpretive Near-Infrared Spectroscopy

The energy absorbed by a matrix consisting of organic compounds depends upon the chemical composition of the matrix, defined by the species (or type) of molecule present, the concentration of these individual species, and the interactions between the molecules in the matrix. For NIR (or any other vibrational spectroscopic measurement technique) to be valid one must be absolutely assured that different types of molecules absorb at unique frequencies. Due to the broadband nature of NIR spectra, consisting of overlapping combination and overtone bands, the individual species are not well resolved as they are in the mid-infrared region. In addition, many compounds absorb NIR energy throughout the entire wavelength region

making it difficult, if not impossible, to clearly resolve a usable baseline for simple peak height or peak area quantitative methods. This brings one to the same conclusion drawn by early investigators that the NIR region is not especially useful as a quantitative measurement technique. At the very least, novel techniques for spectral manipulation were required to “interpret” the poorly resolved bands and “compensate” for background interferences.

## 1.24 Group Frequencies

Frequencies that are characteristics of groups of atoms (termed *functional groups*) are given common group names and can be assigned general near-infrared locations (in nanometers) for major groups associated with stretching vibrational bands. The locations for the fundamental frequencies, overtones, and combination bands are provided within the text of this chapter. Workman and Coates<sup>6</sup> and Goddu and Delker<sup>7</sup> provide a rich source of information as to locations of fundamental frequencies for the major function groups (see Table 1.5 for examples) within the infrared and near-infrared regions.

## 1.25 Coupling of Vibrations

Coupling indicates that the oscillators or molecular vibrations of two or more molecules are interactive, so that the original vibrational energy states (if the vibrations could occur independently of one another) result in split energy states due to the interaction of the vibrations. Coupling is divided into two basic orders: first and second (Fermi resonance). First-order coupling can be involved in several important infrared group frequencies. For example, CO<sub>2</sub> has the two separate (uncoupled oscillators) of C=O, each occurring at approximately 5405 nm ( $\nu$  at  $\sim 1850\text{ cm}^{-1}$ ), 2756.6–2972.8 nm (2 $\nu$ ), 1855.7–2071.9 nm (3 $\nu$ ), and 1405.3–1621.5 nm (4 $\nu$ ). The interactive (coupled oscillators) energy states occur at 4257 nm ( $\nu$  at  $2349\text{ cm}^{-1}$ , asymmetric stretch), 2171.1–2341.4 nm (2 $\nu$ ), 1461.6–1631.9 nm (3 $\nu$ ), and 1106.8–1277.1 nm (4 $\nu$ ); and 7463 nm ( $\nu$  at  $1340\text{ cm}^{-1}$ , symmetric stretch), 3806.1–4104.7 nm (2 $\nu$ ), 2562.3–2860.8 nm (3 $\nu$ ), and 1940.4–2238.9 nm (4 $\nu$ ). First-order coupling is involved for multiple infrared group frequencies including:<sup>8</sup>

Stretches for all cumulated double bonds,  $X=Y=Z$ ,  
for example,  $C=C=$

Stretches in XY<sub>2</sub>, including -CH<sub>2</sub>-, and H<sub>2</sub>O

Stretches in XY<sub>3</sub> groups, including -CH<sub>3</sub>

Deformations of XY<sub>3</sub> groups, including -CH<sub>3</sub>, CCl<sub>3</sub>

N-H in-plane bend of secondary amides, for example,  
R-CO-NH-R'

## 1.26 Fermi Resonance (or Second-Order Coupling)

Fermi resonance<sup>9</sup> is the interaction or coupling of two vibrational energy states with resultant separation of the states where one of the states is an overtone or a sum tone. An overtone vibration occurs as the integer multiple of a fundamental vibration in frequency space (intensity falls off rapidly with the higher multiples):

The first overtone of a fundamental vibration ( $\nu$ ) is equal to  $2 \times \nu$ .

The second overtone of a fundamental vibration is equal to  $3 \times \nu$ .

The third overtone is equal to  $4 \times \nu$ .

Note: Overtones are a special case of sum tones where the frequencies are identical. A sum tone is the general case of an overtone where the frequencies are not equal and where a variety of vibrational energy states can occur:

A binary sum tone is equal to the sum of two fundamentals, for example,  $\nu_i + \nu_k$ .

A ternary sum tone is equal to the sum of three fundamental vibrations, for example,  $\nu_i + \nu_k + \nu_m$ .

Other sum tones can occur such as the sum of an overtone and a fundamental vibration, for example,  $2\nu_i + \nu_k$ .

Three requirements are stated for Fermi resonance.<sup>8</sup>

The zero-order frequencies must be close together (typically within  $30\text{ cm}^{-1}$ ).

The fundamental and the overtone or sum tone must have the same symmetry.

There must be a mechanism for the interaction of the vibrations.

Note: (1) The vibrations cannot be separate (or localized) in distinctly different parts of the molecule. (2) The vibrations must be mechanically interactive in order that the interaction of one vibration affects another.

**Table 1.5 Example Functional Group Names and General Formulas in Simplified Molecular Input Line Entry Specification (SMILES) Format**

| Hydrocarbons, etc.   | Ethers   |
|--|--|
| C-C, paraffinics (or alkanes)  | -OCH <sub>3</sub> , methoxy (or ether group)                                     |
| CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>N</sub> -CH <sub>3</sub> , normal paraffins | C-O-C, ethers  |
| R-CH <sub>3</sub> , methyl C-H   | <b>Hydroxy</b>   |
| R-CH <sub>2</sub> R', methylene C-H  | -OH, hydroxyl-[O-H]  |
| R-CHR'R'', methine C-H   | R-OH, alcohols [O-H]   |
| C1CCCCC1, cyclohexane  | -CH <sub>2</sub> -OH, primary alcohols:  |
| >C=C<, olefinic group (or alkenes)   | R'R''CH-OH, secondary alcohols   |
| -CH=CH <sub>2</sub> , vinyls   | R'R''R'''C-OH, tertiary alcohols   |
| R'R''C=CH <sub>2</sub> , vinylidenes   | Ar-OH, phenolics (or phenols) [O-H]  |
| >C=C=CH <sub>2</sub> , allenes   | Ar=C1CCCCC1  |
| -C≡C-, acetylenes (or acetylinics)   | <b>Nitrogen Compounds</b>  |
| C <sub>N</sub> H <sub>N</sub> , aromatics  | -C≡N, or C#N, nitriles   |
| C <sub>N</sub> H <sub>2N</sub> , naphthalenes (or cycloalkanes)                      | R-C≡N-, or R-C#N-, nitriles  |
| <b>Carbonyl Compounds</b>  | S-C≡N-, or S-C#N-, thiocyanate   |
| R-C(=O)-H, aldehydes   | C≡N-, or C#N, cyanide  |
| R-C(=O)-R', ketones  | C-NO, nitroso-group  |
| >C=C<HC(=O)-R', ketenes  | R'R''NNO, nitrosamines   |
| R-C(=O)-OR', esters  | R-NO <sub>2</sub> , nitro-group (or nitrite)                                     |
| S-C(=O)-O-R', thiol esters   | R-NH <sub>2</sub> , primary amines   |
| R-C(=O)-C(=O)-R, anhydrides  | R'R''NH, secondary amines  |
| -C-O-O-C-, peroxides   | R-NH <sub>3</sub> <sup>+</sup> , R'R''NH <sub>2</sub> <sup>+</sup> , amine salts |
| -O-C(=O)-C(=O)-O-, oxalates  | N=N, azo-group   |
| -O-C(=O)-, carboxy-  | -N=N+=N-, -N=N+=N; azides  |
| -C(=O)-, carbonyl group  | NNO, azoxy group   |
| -C(=O)-NH <sub>2</sub> , primary amides  | R-O-N-N=O, organic nitrites  |
| -C(=O)-NHR, secondary amides   | -NO <sub>3</sub> , nitrates  |
| -C(=O)-NR'R'', tertiary amides   | ON=NO, nitroso-group   |
|  | H <sub>3</sub> N <sup>+</sup> -CH-C(=O)O <sup>-</sup> , amino acids              |

The results of Fermi resonance are important for infrared and near-infrared spectroscopy. Fermi resonance causes the following effects on spectral bands:

The resultant bands are moved in position from their expected frequencies.

Overtone bands are more intense than expected.

There may exist doublet bands where only singlets were expected.

Solvent changes can bring about slight shifts in frequency location of a band and intensities can be greatly changed.

## 1.27 Tools and Techniques for Assigning Band Locations

There are many current techniques used for assisting in near infrared band assignments, including Darling–Dennison<sup>10</sup> resonance, deuteration, polarization, and 2D correlation spectroscopy. The scope of this book is practical rather than theoretical, and so the techniques are mentioned here for further investigation by the reader.

For some molecules, for example H<sub>2</sub>O, the near-resonant frequencies of the symmetric (*s*) and asymmetric (*a*)

stretches interact in such a way that the normal stretching modes in the molecule couple. Addition of the Darling–Dennison coupling in a molecule gives a band that is no longer separable into the two *s* and *a* modes. The Darling–Dennison coupling is for two modes *s* and *a* that have approximately the same frequency, which is often called a 1:1 resonance coupling.

Heavy hydrogen or deuterium is also used to deuterate compounds and correlate the changes in their near-infrared spectral band positions, intensities, and widths for both the deuterated (deuterium-labeled) and undeuterated (unlabeled) molecules. This experiment provides information for the identification of the vibrational modes of the deuterated molecule based on the known or accepted assignments of the nondeuterated molecular forms.

Polarization and dichroism methods, such as variable circular dichroism (VCD) and magnetic circular dichroism (MCD), are used to determine band assignments in complex molecules. By using various models, polarization features can be correlated with the observed positions of bands in the near-infrared spectra. Absorption bands are assigned to short-axis polarized Q transitions measured using such techniques.

Two-dimensional (2D) correlation spectroscopy is used for detailed band assignment work. The technique allows spectral information to be analyzed that is much richer in information content than one-dimensional data. Cross-correlation analysis methods are applied to spectral combinations of NIR with NIR or NIR and mid-IR allowing band assignments to be more easily accomplished. An excellent review paper describing the mathematics used in 2D correlation spectroscopy along with several examples

of generalized 2D NIR and 2D NIR–mid IR heterospectral correlation analysis are introduced with 42 references by Ozaki and Wang.<sup>11</sup>

More recently, intracavity dye laser photoacoustic absorption spectra of molecules has been used for experimental and ab initio investigation of the overtone vibrations in selected molecules.<sup>12</sup>

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# Chapter 2

## **Alkanes and Cycloalkanes**



## 2.1 C-H Functional Groups

The fact that aliphatic hydrocarbons had an absorption band at 1.7  $\mu\text{m}$  was known as early as 1881.<sup>1</sup> The assignment of this absorption as a first overtone of a C-H stretch vibration was perhaps first recognized by Joseph Ellis, although he initially felt that the 1.7  $\mu\text{m}$  peak was part of a harmonic series that began with the 6.9  $\mu\text{m}$  CH bending mode.<sup>2</sup> Nevertheless, the assignment of the first overtone of carbon-hydrogen stretching vibrations was made very early in the history of near-infrared spectroscopy.

Aliphatic and aromatic C-H stretching first overtones are rich in information content, having much the same information as the fundamental vibrations. In addition, the combinations of these stretches with other vibrational modes provide much of the spectral structure of the near-infrared region.

As a general assignment, the first overtones of C-H stretching occur between 5555 and 5882  $\text{cm}^{-1}$  (1700–1800 nm), the second overtones between 8264 and 8696  $\text{cm}^{-1}$  (1150–1210 nm), and the third overtones between 11364 and 10929  $\text{cm}^{-1}$  (880–915 nm). The most important combination regions occur between about 6666 and 7690  $\text{cm}^{-1}$  (1300–1500 nm), and 4545 and 4500  $\text{cm}^{-1}$  (2200–2500 nm).

## 2.2 Methyl Groups, $\text{CH}_3$

Figure 2.1 shows an example with some general band assignments of the methyl C-H spectral regions for iso-octane (2,2,4-dimethyl pentane), a molecule that has mostly methyl groups.

### 2.2.1 First Overtone Region

As seen in Figure 2.2, a homologous series of alkanes has four main peaks in the first overtone region. In the mid-infrared fundamental region, these peaks represent the methyl asymmetric, methylene asymmetric, methyl symmetric, and methylene symmetric vibrations in order from highest to lowest wavenumber. In the near infrared, however, their actual assignments are more complex. As shown in Figure 2.2, the two lower wavelength (higher wavenumber) peaks decrease as the chain length increases, clearly indicating that these two belong to the methyl group.

As described by Tosi and Pinto,<sup>3</sup> who examined 50 linear and branched hydrocarbons, there are five primary bands in the first overtone region. The first appears at  $5905 \pm 4 \text{ cm}^{-1}$  in all of the hydrocarbons and can be attributed to the

methyl group. It is probably related to the first overtone of the asymmetric stretch of the methyl group. The position of the second peak decreases in wavenumber with an increase in chain length and follows the formula:  $5853 + 49F\text{-CH}_3$ , where  $F\text{-CH}_3$  is the mole fraction of methyl groups in a given hydrocarbon. For hexane, for example, this peak would be estimated to be at  $\sim 5870 \text{ cm}^{-1}$ . As seen in Figure 2.2, the methyl peaks of hexane are at 5907 and 5870  $\text{cm}^{-1}$ . The second peak appears to be initially stronger, but it becomes less distinct when the chain length is increased as the neighboring methylene peak affects it.

Within the classes of hydrocarbon compounds (linear, singly branched, doubly branched), good correlations between the peak intensities and the percent of the functional group can be obtained. In general, the absorptivity of terminal methyls is higher than that of internal or branched methyls.

As in the mid-infrared, adjacent atoms can affect the position of the C-H stretch vibrations. Table 2.1 lists some examples. Figure 2.3 illustrates the shift of the two methyl “overtone” peaks with the influence from the carbonyl group.

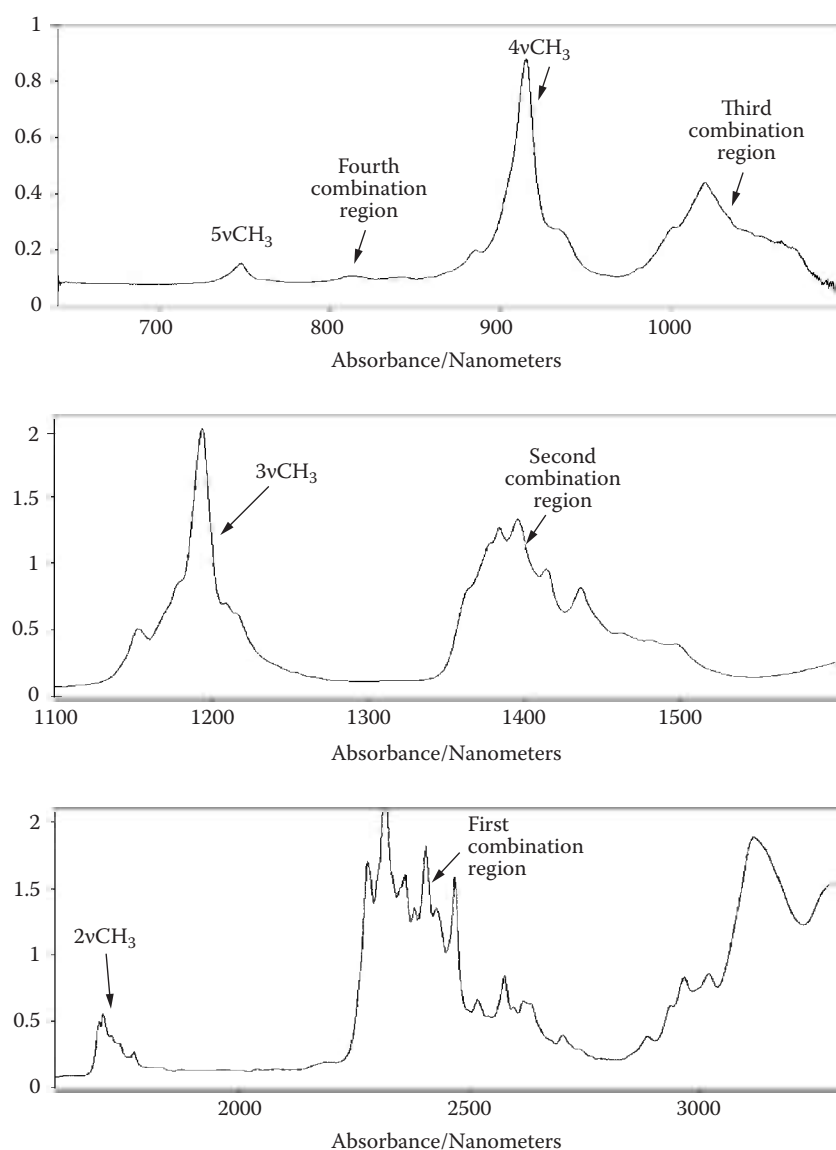
In addition to the two methyl peaks near 5790 and 5735  $\text{cm}^{-1}$ , the methyl group in aromatic compounds has a band near 5660  $\text{cm}^{-1}$ , which has been found useful for quantitative analysis. Luty and Rohleder<sup>4</sup> assigned this peak to be due to  $\nu_a + 2\delta_a$ . They also suggest that a peak at 4080  $\text{cm}^{-1}$  is due to  $3\delta_s$ , the second overtone of a symmetric bending vibration of the  $\text{CH}_3$  group. This peak is well isolated in compounds having multiple methyl groups, such as penta and hexamethyl benzene.

### 2.2.2 Higher-Order Overtones

As seen in Figure 2.1, the second, third, and fourth overtone regions (3v, 4v, and 5v) have only one strong band. This was thought to be most likely due to the asymmetrical vibrations, as the symmetrical bands became relatively weaker in higher overtones.<sup>5</sup> An alternate theory for this phenomenon is that local mode effects at the higher overtones combine to create only one general absorption peak. The second overtone is generally considered intermediate between the normal mode and local mode, whereas the higher-order overtones are only local mode.

The second overtone region (1150–1210 or 8264–8696) has also been used for quantitative measurements, in particular to measure methyl, methylene, methine, and aromatic





**FIGURE 2.1** Illustration of aliphatic C-H (as predominantly methyl C-H str.) from 2,2,4-dimethyl pentane (isooctane). The top spectrum (from left to right) shows the fourth overtone (5v), the third overtone (4v), and combination bands. The center spectrum illustrates the second overtone (3v) and combination bands. The bottom spectrum presents the first overtone (2v) and combination bands, and a portion of the fundamental. (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. 1996, 31(3), 277. With permission.)

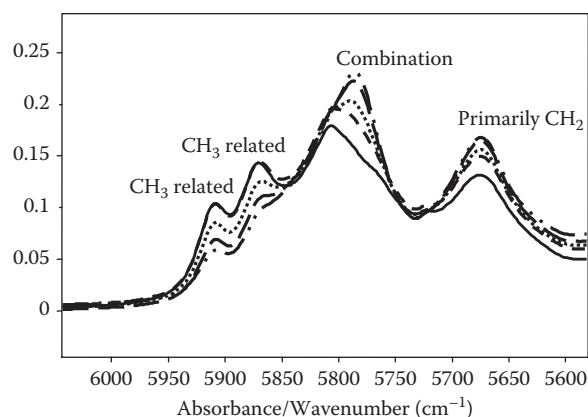
contributions.<sup>6</sup> The methyl groups of long-chain paraffinic hydrocarbons appear between 8365 and 8375  $\text{cm}^{-1}$  (1194–1195).<sup>7</sup> In pentane and hexane, the methyl group absorbs at 8396  $\text{cm}^{-1}$  (1191 nm), in heptane it absorbs at 8388  $\text{cm}^{-1}$  (1192 nm), and in decane it is at 8378  $\text{cm}^{-1}$  (1194 nm). See Figure 2.4.

The third overtone vibration of the methyl group appears at 10953  $\text{cm}^{-1}$  in hexane. The methyl third overtone in some additional molecules is listed in Table 2.2.<sup>8</sup> Wheeler assigns

the fourth overtone's position to be at about 13400  $\text{cm}^{-1}$  (746 nm).<sup>9</sup> Fang and Swofford also list the fifth overtone for a linear alkane methyl group CH stretch to be at 15690  $\text{cm}^{-1}$  (637 nm), and the sixth at about 17890  $\text{cm}^{-1}$  (560 nm).<sup>10</sup>

### 2.2.3 Combination Bands

The first “combination” region near 4500–4545  $\text{cm}^{-1}$  (2200–2500 nm) is rich in information but complex, as it includes combinations of CH stretching with various



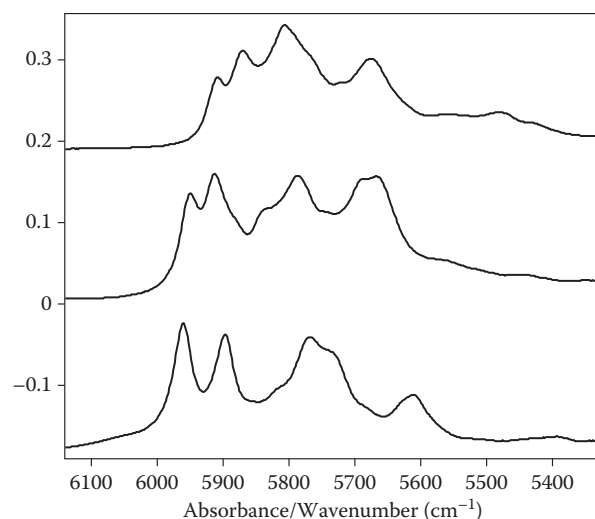
**FIGURE 2.2** First overtones of methyl and methylene CH stretching; solid line is hexane, small dash heptane, dots nonane, long dash dodecane, and dot-dash hexadecane. (From Weyer, L.G. and Lo, S.-C., *Spectra-Structure Correlations in the Near-Infrared in Handbook of Vibrational Spectroscopy*, Chalmers, J. C., and Griffiths, P. R., Eds., John Wiley & Sons, 2002. With permission.)

**Table 2.1** Peak Positions for the Methyl Group in the 5000–6000  $\text{cm}^{-1}$  Region

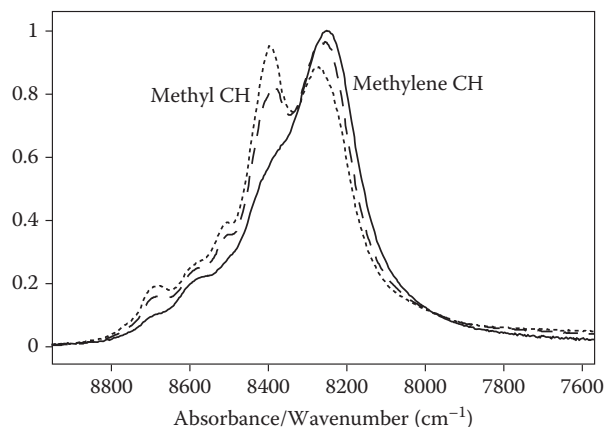
|  |  |
|--|--|
| Aliphatic, terminal $\text{R-CH}_3$<br>terminal  | 5905, 5853 + 49 $\text{F-CH}_3$  |
| Aliphatic, branched $\text{CH}_3$<br>$\text{-R-CH-R-}$   | 5905, 5872   |
| Aromatic   | 5790, 5735, plus 5650  |
| Carbonyl $\begin{array}{c} \text{O} \\    \\ \text{-C-CH}_3 \end{array}$                                   | 5960, 5898   |
| Carbonyl, one carbon removed $\begin{array}{c} \text{O} \\    \\ \text{-C-CH}_2\text{CH}_3 \end{array}$    | 5946, 5908   |
| Hydroxyl, $\text{HO-CH}_3$   | 5880, 5773   |
| Ether, $\text{CH}_3\text{-O-CH}_3$   | 5880, 5770   |
| Amine  |  |
| Halogen $\begin{array}{l} \text{CH}_3\text{Cl} \\ \text{CH}_3\text{Br} \\ \text{CH}_3\text{I} \end{array}$ | 6000/6040 doublet, 5882 – gas<br>6025/6060 doublet, 5900 – gas<br>6020, 5902, 5845 |
| Nitro $\text{-NO}_2$   | 6045, 5874   |

bending and stretching vibrations from the mid-infrared “fingerprint” region. In addition, overtones of bending modes alone may be present.

For the methyl functional group, there is a strong peak near  $4395\text{ cm}^{-1}$  (2275 nm), as seen in Figure 2.5. This is probably a  $\nu + \delta$  combination. There is also said to be



**FIGURE 2.3** Shift of methyl overtone peaks; top spectrum is hexane, middle is 3-pentanone, and bottom is acetone.



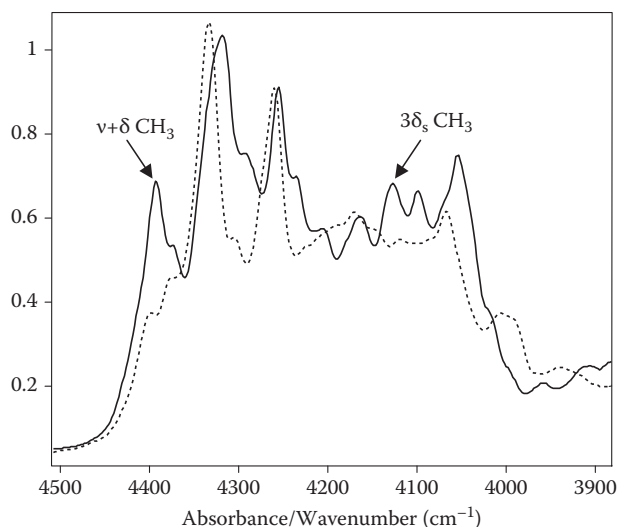
**FIGURE 2.4** Second overtone region, illustrating the separation of methyl and methylene contributions. The figure shows hexane (dotted curve), octane (dashed), and octadecane (solid).

a  $3\delta$  peak of the symmetric methyl bending “umbrella” vibration near  $4100\text{ cm}^{-1}$  (2410–2460 nm).<sup>11,12</sup> A  $3\delta$  overtone of the asymmetric bending mode is expected to be at  $4400\text{ cm}^{-1}$  (2270 nm). A third overtone of the symmetric bending vibration,  $4\delta$ , is cited at about  $5520\text{ cm}^{-1}$  (1812 nm), while a third overtone of the asymmetric bending vibration is suggested to be at  $5814\text{ cm}^{-1}$  (1720 nm).

In the  $7100\text{ cm}^{-1}$  (1400 nm) region of second combination bands, the double peak probably near  $7355\text{ cm}^{-1}$  (1360 nm) and  $7263\text{ cm}^{-1}$  (1377 nm) is suggested to be a combination of  $2\nu + \delta$ .<sup>12</sup> Also, in branched dimethyl alkanes, there is

**Table 2.2 Example Third Overtone Methyl Peaks**

| Compound                    | Peak Position (cm <sup>-1</sup> ) | Peak Position (nm) |
|-----------------------------|-----------------------------------|--------------------|
| 1-Bromoalkane               | 10953                             | 912                |
| 1-Heptene                   | 10953                             | 912                |
| n-Hexane                    | 10953                             | 912                |
| 1-Amino hexane              | 10941                             | 914                |
| 2-Amino propane             | 10977                             | 911                |
| Propionaldehyde             | 11052                             | 905                |
| 3-Chloro-2-methyl-1-propane | 10965                             | 912                |
| 1-Octanol                   | 10953                             | 912                |
| Toluene                     | 10977                             | 911                |
| Ethylbenzene                | 10953                             | 912                |

**FIGURE 2.5** First combination region of 2,5-dimethyl hexane (solid line) and decane (dashed line).

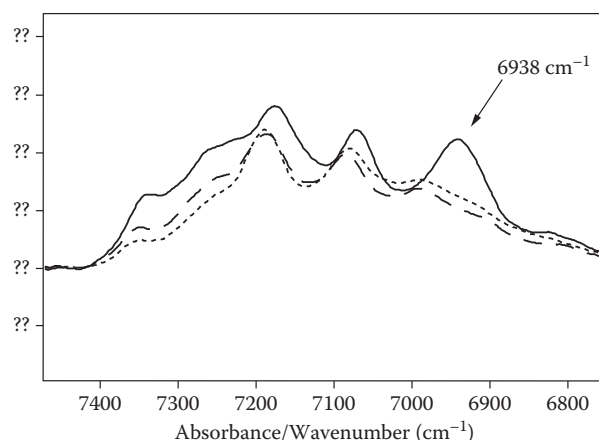
another, larger peak at 6938 cm<sup>-1</sup> (1440 nm). This is shown in Figure 2.6.

## 2.3 Methylene Groups, CH<sub>2</sub>

The general absorptions of methylene groups are illustrated in Figure 2.7, a spectrum of n-decane.

### 2.3.1 First Overtone Region: Linear Molecules

Methylene groups in linear, aliphatic molecules have two primary peaks at about 5800 cm<sup>-1</sup> (1723 nm) and 5680 cm<sup>-1</sup>

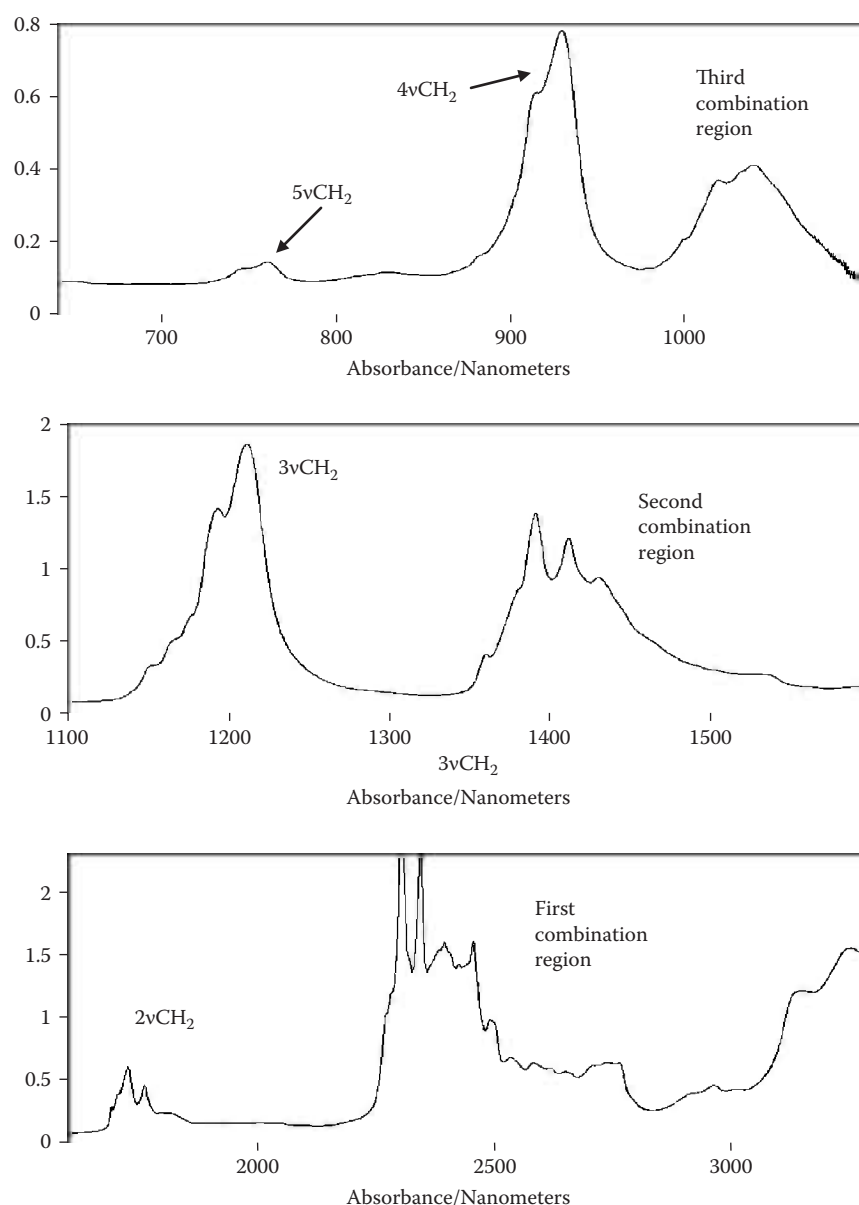
**FIGURE 2.6** Illustration of branched hydrocarbon second combination band: 2,5-dimethyl hexane (solid line), hexane (dashed line), and decane (dotted line).

(1762 nm) in the first overtone region. The 5800 cm<sup>-1</sup> nm peak is generally thought to be a combination band,<sup>14</sup> reported as  $\nu_a + \nu_s$ .<sup>14</sup>

The 5800 cm<sup>-1</sup> peak is usually the strongest peak in the first overtone region of a series of linear hydrocarbons. Tosi and Pinto<sup>3</sup> provide a formula for locating this peak for a series of linear hydrocarbons:  $5856 - 85 \times \text{Weight fraction of CH}_2$ , or about 5800 cm<sup>-1</sup> for hexane. They also mention that this peak splits into two, closely spaced peaks possibly due to the influence of adjacent methyl groups. The absorptivity of this combined peak does not regularly increase with chain length, probably because it has contributions from two sources.

The weaker methylene peak in the first overtone region was said to be at  $5671 \pm 3$  cm<sup>-1</sup> for linear hydrocarbons. This peak was thought to have contributions from both methyl and methylene groups,<sup>3</sup> although others have assigned a 5680 cm<sup>-1</sup> band to be both the first overtone of the methylene symmetric stretch and of the asymmetric stretch shifted by Fermi resonance.<sup>13</sup> More recently, Parker et al.<sup>15</sup> have discussed the origins of this peak in terms of local mode theory.

In the second overtones, which are also shown in Figure 2.7, only one methyl and one methylene peak are normally observed at 8389 cm<sup>-1</sup> (1192 nm) and 8264 cm<sup>-1</sup> (1210 nm), although weaker peaks can be seen at 8673 cm<sup>-1</sup> (1153 nm) and 8503 cm<sup>-1</sup> (1176 nm) with higher resolution. In higher alkanes, above dodecane, the methyl group becomes a shoulder in the methylene peak.<sup>16</sup>



**FIGURE 2.7** Illustration of aliphatic C-H (as predominantly methylene C-H str.) from n-decane. The top spectrum (from left to right) shows the fourth overtone (5v), the third overtone (4v), and combination bands. The center spectrum illustrates the second overtone (3v) and combination bands. The bottom spectrum presents the first overtone (2v) and combination bands and a portion of the fundamental. (From Workman, J., *Interpretive spectroscopy for near-infrared*, Appl. Spectrosc. Revs. **1996**, 31(3), 277. With permission.)

### 2.3.2 Higher-Order Overtones: Linear Molecules

The second overtone of the methylene CH stretch absorption occurs at  $8284\text{ cm}^{-1}$  (1207 nm) in pentane,  $8271\text{ cm}^{-1}$  (1209 nm) in hexane,  $8256\text{ cm}^{-1}$  (1211 nm) in heptane, and  $8247\text{ cm}^{-1}$  (1212 nm) in decane. The third overtone is at

$10764\text{ cm}^{-1}$  (928 nm) in hexane. The peak positions of some additional compounds are provided in Table 2.3 from Salzer et al.<sup>8</sup> The fourth overtone is at about  $13,100\text{ cm}^{-1}$  (762 nm). Fang and Swofford also list the fifth overtone for a linear alkane methylene group CH stretch to be at  $15400\text{ cm}^{-1}$  (649 nm), and the sixth at about  $17535\text{ cm}^{-1}$  (570 nm).<sup>10</sup>

**Table 2.3 Peak Positions of Additional Model Compounds for Comparison**

| Compound        | Peak Position (cm <sup>-1</sup> ) | Peak Position (nm) |
|-----------------|-----------------------------------|--------------------|
| 1-bromoalkane   | 10764                             | 929                |
| 1-Heptene       | 10787                             | 927                |
| n-Hexane        | 10776                             | 928                |
| Propionaldehyde | 10787                             | 927                |
| 1-Octanol       | 10776                             | 928                |
| Ethyl benzene   | 10753                             | 930                |
| 1-Amino-hexane  | 10753                             | 930                |

### 2.3.3 Combination Bands: Linear Molecules

The two largest peaks in the first combination region seen in Figure 2.6 are due to the asymmetric and symmetric methylene stretching and bending combinations.<sup>13</sup> The asymmetric combination is at 4336 cm<sup>-1</sup> in butane, 4334 in pentane, and 4332 in heptane, whereas the symmetric one is at 4257 in butane, 4262 in pentane, and 4259 in heptane, according to Ricard-Lespade et al.<sup>13</sup>

In an examination of the spectrum of methylene chloride as interpreted by Kaye,<sup>17</sup> the methylene combination peaks at 3945, 4196, 4253, and 4453 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> are explained as  $\nu + \delta$  combinations as listed in Table 2.4. The analogous bands in a normal hydrocarbon would be at about 4068, 4168, 4261, and 4333 cm<sup>-1</sup>.

In the second combination region, shown in Figure 2.7, there is a doublet relating to the methylene group, the larger peak, at about 7186 cm<sup>-1</sup> (1391 nm) and the smaller at about 7080 cm<sup>-1</sup> (1412 nm). This doublet has been attributed to  $2\nu + \delta$ .<sup>12</sup> The  $2\nu$  term is neither asymmetric nor symmetric, as the vibrations are uncoupled at this

**Table 2.4 First Combinations Bands of Methylene Groups in CH<sub>2</sub>Cl<sub>2</sub>**

| Assignment         | Peak Observed (cm <sup>-1</sup> ) | Peak Calculated | Summation   |
|--------------------|-----------------------------------|-----------------|-------------|
| $\nu_a + \delta_r$ | 3945                              | 3951            | 3055 + 896  |
| $\nu_a + \delta_t$ | 4196                              | 4211            | 3055 + 1156 |
| $\nu_s + \delta_w$ | 4253                              | 4251            | 2987 + 1264 |
| $\nu_a + \delta_b$ | 4453                              | 4477            | 3055 + 1422 |

Note: r, rocking vibration; t, twisting; w, wagging; b, bending.

point. Kaye called it  $\nu_a + \nu_s$ . Also,  $\delta$  would include rocking, twisting, and bending vibrations. The two strongest bands are probably  $2\nu + \delta_b$  and  $2\nu + \delta_t$ , based on Kaye's description of the spectrum of methylene chloride.<sup>17</sup>

There are also a number of weaker combination bands in the area between the first combination and the first overtones regions, 4500–5500 cm<sup>-1</sup> or about 1800 to 2220 nm. These include  $\nu_a + 2\delta_r$ ,  $\nu_s + \delta_r + \delta_t$ ,  $\nu_s + 2\delta_t$ , and  $\nu_a + \delta_r + \delta_t$ .

### 2.3.4 First Overtones: Cyclic Molecules

The first overtone stretching vibrations of methylene groups of strained-ring cyclic compounds such as cyclopropane occurs near 6135 cm<sup>-1</sup> (1630 nm). Several authors have studied the effects of various substituents on the ring. Gassman and Zalar list the band positions of 37 cyclopropane derivatives.<sup>18</sup> Gassman also published a table of first overtone CH band positions of aliphatic norbornene derivatives.<sup>19</sup> These overtones were at slightly lower wave-number maxima than the cyclopropanes, about 6024 cm<sup>-1</sup> (1660 nm).

The CH stretch first overtone region of cyclohexane has two strong peaks at 5697 cm<sup>-1</sup> (1755 nm) and 5791 cm<sup>-1</sup> (1727 nm). A number of smaller, additional peaks were also seen by curve resolution.<sup>20</sup> The two strongest peaks are probably  $2\nu_a$  and  $2\nu_{as}$ ,<sup>21</sup> with the intensity of the symmetric band being intensified by Darling–Dennison resonance.

Cyclopentane, cyclobutane, cyclopropane, and many other cyclic molecules have been studied. In the fundamental region, the frequency increases as the ring becomes more strained, and the first overtones reflect this trend. Cyclopentane's two strongest first overtone peaks are at 5730 cm<sup>-1</sup> (1745 nm) and 5834 cm<sup>-1</sup> (1714 nm) for example, as compared to cyclohexane's 5697 and 5791 cm<sup>-1</sup>.

Inductive effects on cyclopropane's first overtone have been extensively documented.<sup>18,22</sup>

There is a shift from 6158 cm<sup>-1</sup> (1624 nm) to 6060 cm<sup>-1</sup> (1650 nm) in moving from strongly electron-withdrawing groups such as cyano to strongly electron-inducing groups such as methyls.

A terminal epoxy ring is one case in which methylene CH groups are influenced by the strained structure and an oxygen atom. Such epoxides, such as epichlorohydrin and 1,2-diisobutylene oxide have a sharp absorption band at

**Table 2.5 Normal-Mode Band Assignments for Chloroform and Bromoform**

|                 | $\delta$ | $\nu$ | $\nu+\delta$ | $\nu+2\delta$ | $2\nu$ | $2\nu+\delta$ | $2\nu+2\delta$ | $3\nu$ | $3\nu+\delta$ |
|-----------------|----------|-------|--------------|---------------|--------|---------------|----------------|--------|---------------|
| $\text{CHCl}_3$ | 1215     | 3019  | 4215         | 5374          | 5910   | 7090          | 8229           | 8676   | 9836          |
| $\text{CHBr}_3$ | 1143     | 3020  | 4145         | 5240          | 5907   | 7024          | —              | 8677   | 9760          |

about  $6060\text{ cm}^{-1}$  (1650 nm) with a molar absorptivity of about  $0.2\text{ L/mole}\cdot\text{cm}$ .<sup>23</sup>

### 2.3.5 Higher-Order Overtones: Cyclic Molecules

For cyclohexane, the second overtone of the CH stretch is probably a combination of normal and local mode effects, with the two major bands being related to oscillators localized on the axial and equatorial CH bonds.<sup>24</sup> The larger peak, near  $8290\text{ cm}^{-1}$  for cyclohexane,  $8434\text{ cm}^{-1}$  for cyclopentane, and  $9116\text{ cm}^{-1}$  (1097 nm)<sup>9</sup> for cyclopropane, has been used for characterizing various cyclic structures from petroleum fractions.<sup>7</sup>

Higher overtones of cyclopentane, cyclobutane, and cyclopropane have also been studied, with regard to their information content on equatorial and axial conformations.<sup>25</sup> It is generally acknowledged that these higher overtones are explained by local mode theory.

The second overtone of the CH stretch connected to an epoxy ring has been used for quantitative work.<sup>26</sup> The peak appears at  $8620\text{ cm}^{-1}$  (1160 nm).

### 2.3.6 Combination Bands: Cyclic Molecules

The  $4545\text{ cm}^{-1}$  (2220 nm) combination band of the cyclopropane group has been studied along with the first overtone and has been found to also shift to higher frequencies with electron-withdrawing power.<sup>22,27</sup> The assignment is probably a  $\nu + \delta$  combination.

Terminal epoxides have a similar combination band that has been used for quantitative analysis following the cure of epoxy resins.<sup>28</sup> It appears at about  $4525\text{ cm}^{-1}$  (2210 nm) and has an absorptivity of about  $1.5\text{ L/mole}\cdot\text{cm}$ .<sup>23</sup>

## 2.4 Methine Groups

The absorption of the single methine proton in the presence of methyl and methylenes is generally too small to

be observed and is little mentioned in the literature. In the mid-infrared, the fundamental peak is near  $2900\text{ cm}^{-1}$ , between the methyl and methylene doublets. This would suggest that its first overtone was also in the envelope of small peaks in the  $5882\text{ cm}^{-1}$  (1700 nm)– $5555\text{ cm}^{-1}$  (1800 nm) region.

Wheeler<sup>9</sup> gives the second overtone of an aliphatic methine to be  $8163\text{ cm}^{-1}$  (1225 nm) and a second combination band to be at  $6944\text{ cm}^{-1}$  (1440 nm).

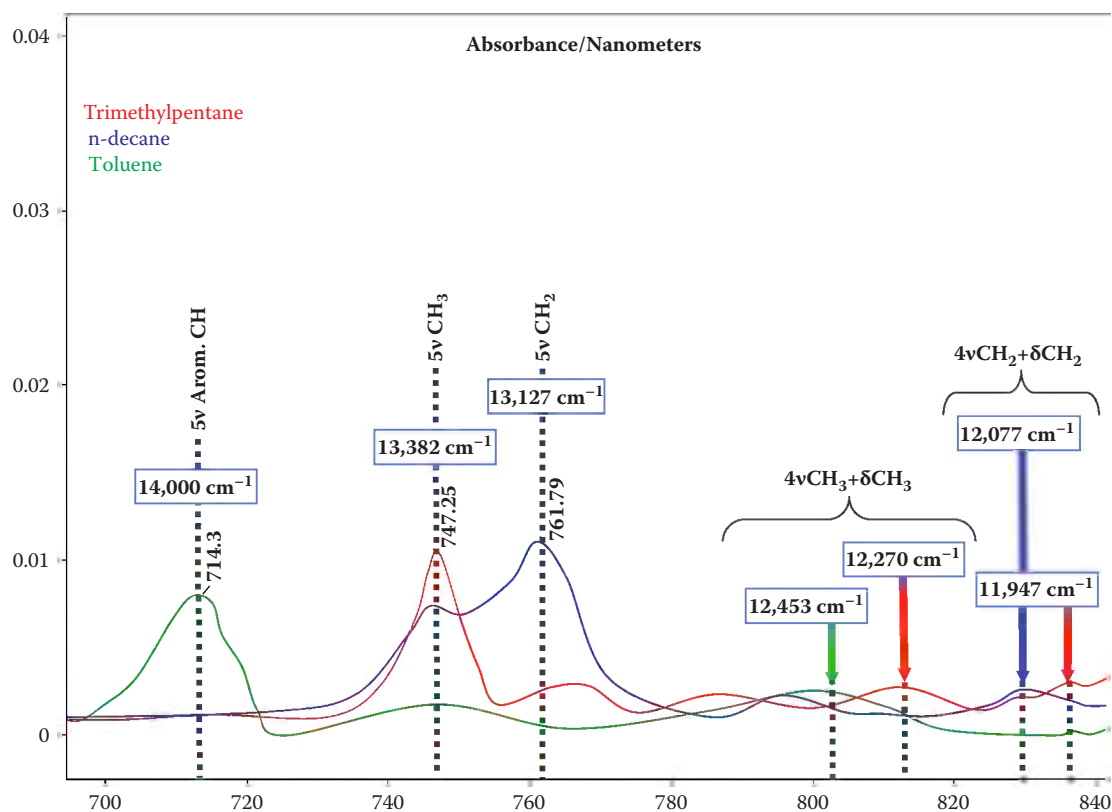
The isolated aliphatic C-H group has been studied in halogenated compounds.<sup>29</sup> The table below lists the band assignments for chloroform and bromoform, expressed in terms of normal modes. The authors mention that some of these bands are split by the nondegeneracy of the deformation vibrations. These assignments are in agreement with those of Kaye.<sup>17</sup>

Iwamoto et al.<sup>29</sup> also discuss the effect of the isolation of the CH group in the  $\text{CHX}_3$  and  $\text{CHX}_2\text{-CX}_2\text{-CHX}_2$  molecules, in comparison with the coupled modes of  $\text{CHX}_2\text{-CHX}_2$  molecules. In the latter case, additional peak splitting is observed.

In general, the spectral features of vibrations of haloalkanes are affected by the mass of the halogen atom and the force constant of the carbon-halogen bond. If a halogen is bound to the same carbon atom as the hydrogen, the neighboring CH overtone bands are shifted to lower wavelength and their intensities are intensified.<sup>9</sup>

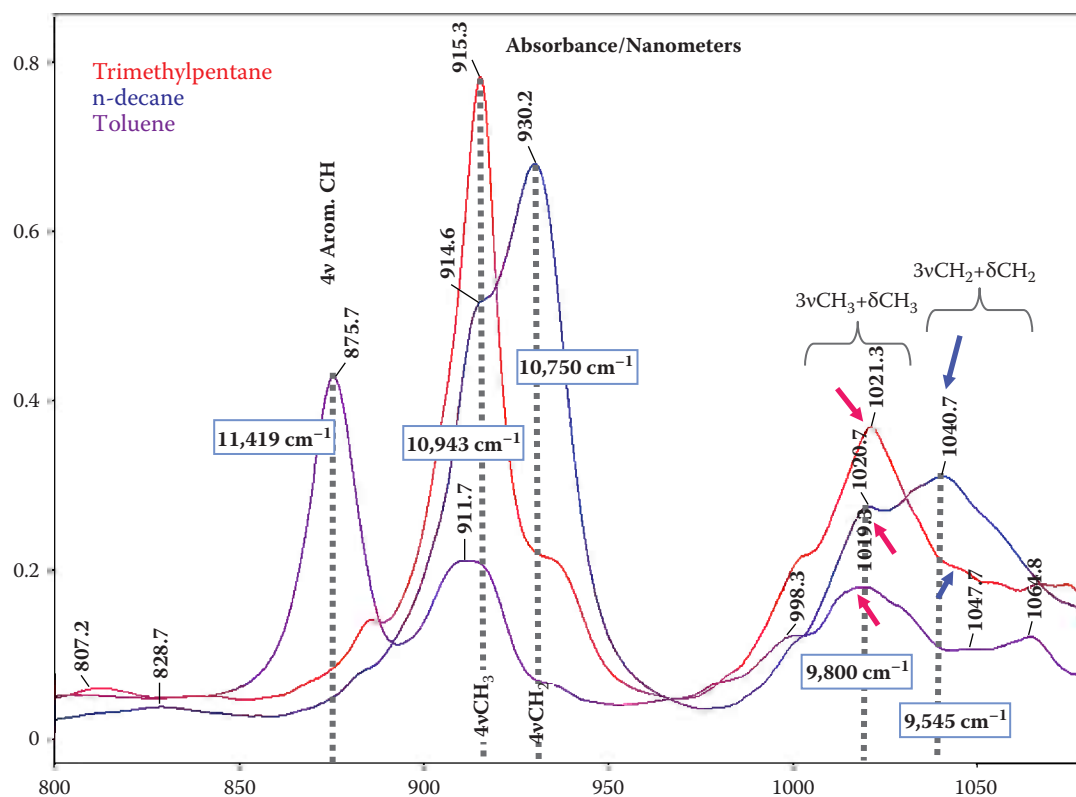
## 2.5 Model Compound Comparisons

Figures 2.8 through 2.12 illustrate the general C-H absorption spectra–structure correlation by using three model compounds: trimethylpentane, n-decane, and toluene. One notes that there are twelve methyl C-H bonds and six methylene C-H bonds in trimethylpentane; and there are six methyl C-H bonds and sixteen methylene C-H bonds in n-decane. In the toluene molecule, there are three methyl C-H bonds, zero methylene C-H bonds, and five aromatic C-H bonds.



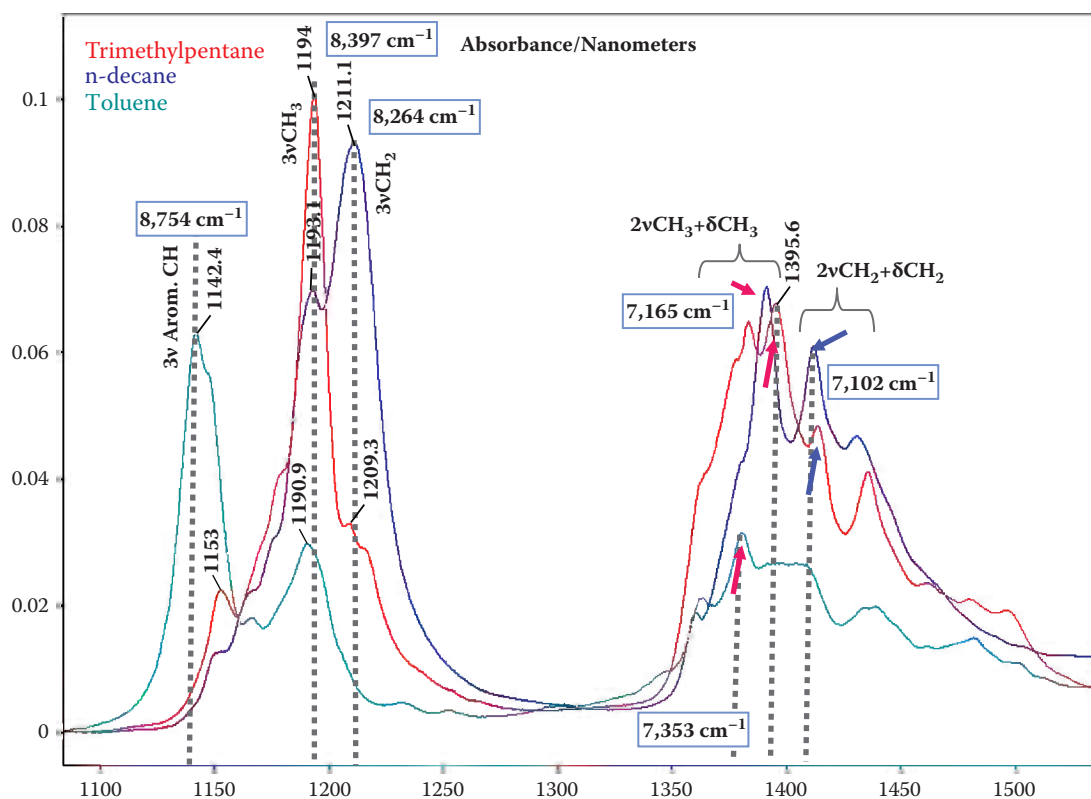
**FIGURE 2.8** The fourth overtone (5v) near-infrared C-H stretch as aromatic C-H, methyl C-H, and methylene C-H stretching band positions in nanometers (nm), with band positions labeled in wavenumbers ( $\text{cm}^{-1}$ ). These are identified as fourth overtone (5v) stretching for methylene, methyl, and aromatic C-H. Within the same figure is shown the third overtone (4v) combination region. For the third overtone (4v) combination region, one observes the methyl stretching and methyl bending combination bands indicated between 800 and 820 nm (12500 to 12195  $\text{cm}^{-1}$ ). One also observes the methylene stretch and the bending combination bands between 830 and 840 nm (12048 to 11905  $\text{cm}^{-1}$ ).



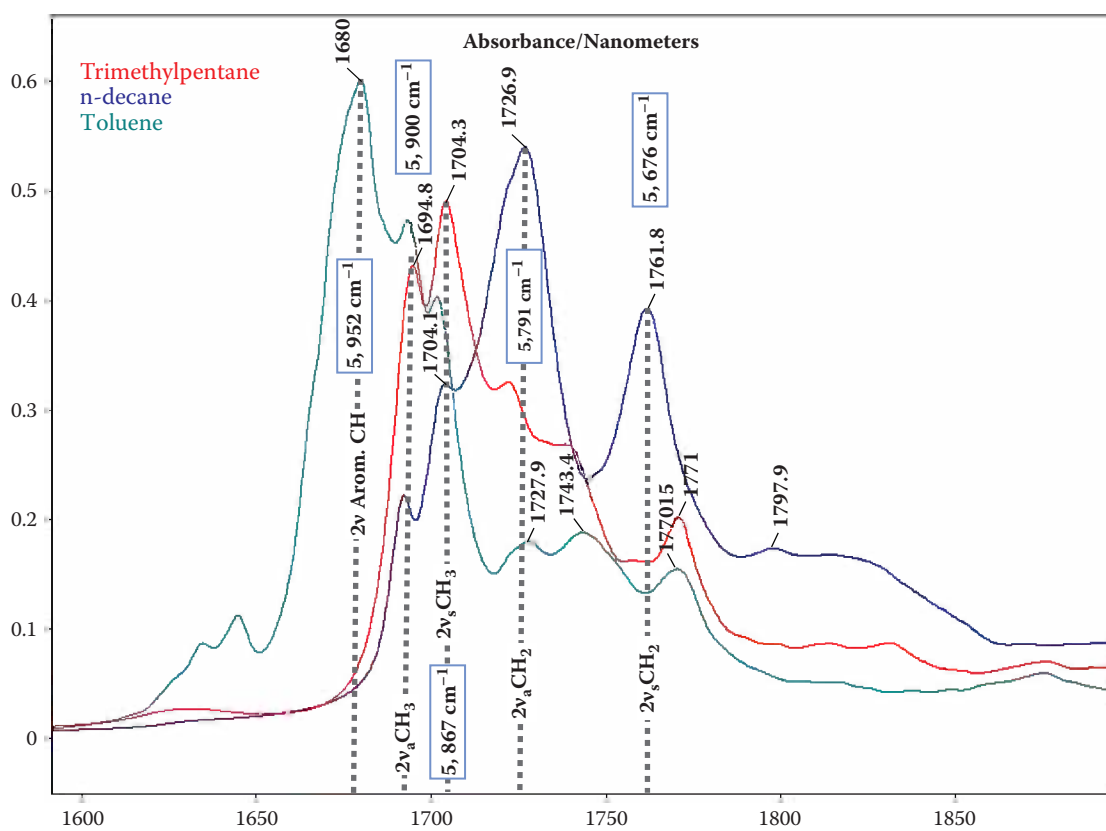


**FIGURE 2.9** The third overtone (4v) harmonic and the second overtone (3v) combination region, illustrating the relative intensities (in AU) and band positions. The third overtone (4v) near-infrared C-H stretching aromatic, methyl, and methylene band positions are shown. The absorption bands are very clearly identified and are very clean absorbance/absorption bands. A region of second overtone (3v) combination bands is also seen in this figure.

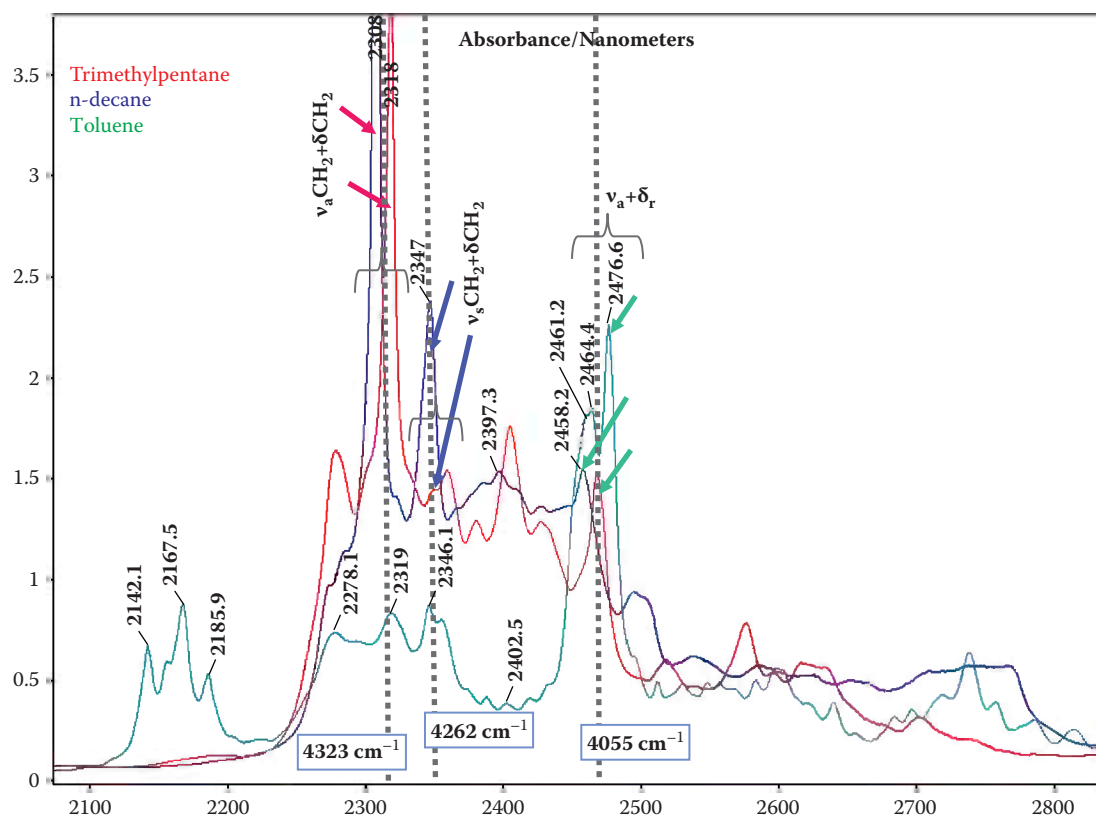




**FIGURE 2.10** The second overtone (3v) spectral region. One also observes the first overtone (2v) stretching and bending combination bands for methyl and methylene as labeled on the figure.



**FIGURE 2.11** A spectrum of the first overtone (2v) spectral region. For these bands we are able to observe both asymmetric and symmetric C-H stretching bands, which were not visible in spectra from the second (3v), third (4v), or fourth (5v) overtone C-H stretching band regions (Figures 2.8 to 2.10). The observable complexity of the (2v) harmonic for the first overtone region demonstrates the presence of significantly more information content (i.e., higher data rank) for this spectral region as compared to the other C-H stretching overtone bands. Within this spectral region one observes the aromatic C-H as a single band, but clearly observes the asymmetric methyl and symmetric methyl stretching as separate bands. We also see that two bands are present for the asymmetric and symmetric methylene stretching. Those are specific and separate bands, and as previously noted can be identified clearly in the first overtone (2v) region but not at higher frequencies.



**FIGURE 2.12** A spectrum of the first combination region for the model compounds. From these spectra of the model compounds one observes the complexity of the combination region starting from about 2100 nm (i.e., 4762  $\text{cm}^{-1}$ ) and extending to near 3000 nm (i.e., 3333  $\text{cm}^{-1}$ ). This spectral region is incredibly complex, and at the time of this publication, there has not been comprehensive assignment work done for each of these particular bands. In a few cases, assignments are labeled in the figure. For example, the asymmetric methylene C-H stretching plus C-H bending combination band is shown near 2308 nm (i.e., 4333  $\text{cm}^{-1}$ ). This figure also shows the symmetric methylene C-H stretching plus C-H bending combination band shown near 2347 to 2350 nm (i.e., 4261 to 4255  $\text{cm}^{-1}$ ). This spectral region is the location for the second overtone (2 $\delta$ ) methyl bending band near 2476 nm (i.e., 4039  $\text{cm}^{-1}$ ). Additional discussion of this spectral region was presented earlier in this chapter.

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# Chapter 3

## **Alkenes and Alkynes**

### 3.1 Linear Alkenes, Overtones

The first overtone of the C-H stretch next to a double bond occurs at a higher wavenumber (lower wavelength) than saturated C-H stretch absorptions. This peak is strong and distinct in some structures, particularly the methylene group of terminal double. In most cases, however, it is weak and difficult to locate especially in the presence of methyl groups. The band position is near 6100–6200  $\text{cm}^{-1}$  (1640–1612 nm).

The CH stretch first overtone of terminal methylene groups of vinyl and vinylidene structures is isolated enough that it can be used in traditional quantitative analysis. Figure 3.1 provides one example and Table 3.1 provides some typical peak locations. Goddu<sup>1</sup> provides tables of absorptivities for the first overtone absorption of the terminal methylene group in a variety of compounds and solvents. Molar absorptivities are about 0.2–0.5 L/mole-cm. Put another way, a 100 ppm amount of methylene gives an absorbance of 0.01 in a 10-cm cell. Analyses using this peak to measure the vinyl content of acrylate monomers,<sup>2</sup> butadienes,<sup>3</sup> and edible oils<sup>4</sup> have been reported.

In studies of wavelength displacement of deuterium substitution, hexadeuteropropylene ( $\text{CD}_3\text{CD}=\text{CD}_2$ ) gives an asymmetric stretching of the  $\text{CD}_2$  at 4610  $\text{cm}^{-1}$  (2170 nm).<sup>5</sup>

In acrylates, in addition to the first overtone near 6000  $\text{cm}^{-1}$  (1665 nm), there is a band at 6167  $\text{cm}^{-1}$  (1620 nm), with overtones at 9020  $\text{cm}^{-1}$  (1109 nm) and 11800  $\text{cm}^{-1}$  (847 nm), used by Gerasimov and Snavelly to study diacrylate and dimethacrylate reactions.<sup>2</sup> Although

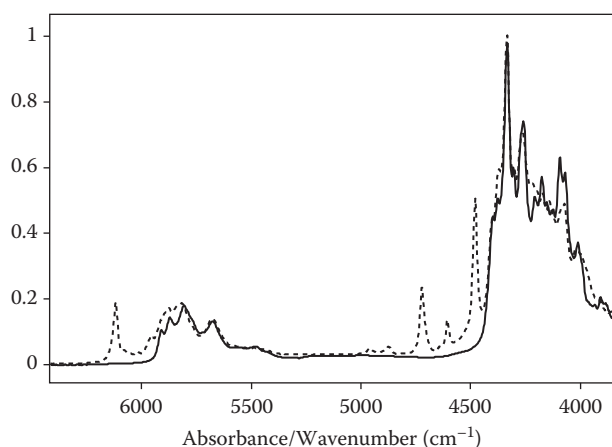


FIGURE 3.1 Hexane (solid) and 1-hexene (dotted).

this is said to be a combination band, it is a combination of two C-H stretch vibrations, rather than a C-H with another type of vibration.

The CH stretch first overtone of a cis double bond has also been found to be distinct. It appears near 5963  $\text{cm}^{-1}$  (1677 nm) and is isolated from the vinyl overtones.<sup>6</sup> Figure 3.2 illustrates the features of cis CH absorptions in comparison to a trans configuration.

The second overtone of the terminal methylene CH stretch can also be used for quantitative analysis. It occurs at about 9260  $\text{cm}^{-1}$  (1080 nm). In 1-alkenes, it is 8897–8944  $\text{cm}^{-1}$  (1118–1124 nm), with a molar absorptivity of 0.004–0.018 L/mole-cm. The peak is at 9017  $\text{cm}^{-1}$  (1109 nm) in allyl stearate and a doublet at 8787–9009  $\text{cm}^{-1}$  (1110–1138 nm) in alkyl acrylates. The peak is at 9091  $\text{cm}^{-1}$  (1100 nm) in alkyl vinyl ethers and about 9059  $\text{cm}^{-1}$  (1104 nm) in vinyl esters.<sup>6</sup>

The third overtone of terminal methylenes' CH stretch is found at 11390  $\text{cm}^{-1}$  (878 nm) in 1-alkenes.<sup>7</sup> Its absorptivity is 0.002 L/mole-cm. The alkyl acrylate doublet occurs at 11905 and 12500  $\text{cm}^{-1}$  (800 and 840 nm). The peak is at 10776–11360  $\text{cm}^{-1}$  (880–928 nm) in alkyl vinyl ethers, and at 10788–10929  $\text{cm}^{-1}$  (915–927 nm) in vinyl ethers and vinyl esters. Fourth through seventh overtones of terminal methylene CH stretch peaks have been studied using photoacoustic spectroscopy.<sup>8</sup> These were given as approximately 11450, 14090, 16630, and 18800  $\text{cm}^{-1}$ , respectively (873, 710, 600, and 532 nm). In the spectrum of propylene, this peak is split into a doublet of two peaks that are cis and trans to the methyl group.

### 3.2 Linear Alkenes, Combinations/Bending Modes

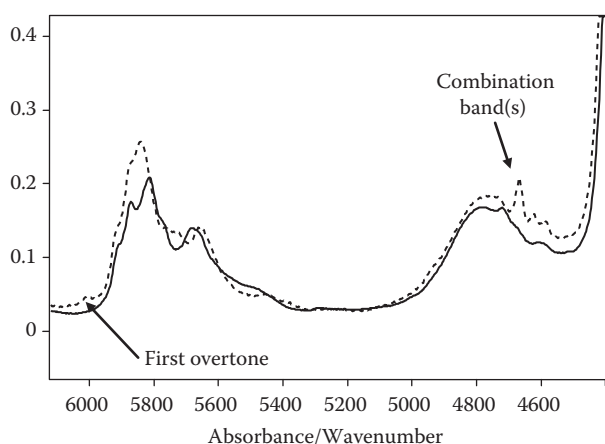
A distinctive set of bands in the combination region exists for vinyl double bonds. As seen in Figure 3.1, there are four peaks at about 4330  $\text{cm}^{-1}$  (2310 nm), 4482  $\text{cm}^{-1}$  (2230 nm), near 4600  $\text{cm}^{-1}$  (2170 nm), and 4670–4780  $\text{cm}^{-1}$  (2090–2140 nm).

The vinyl group in polybutadienes has been studied more extensively than simple alkenes and it has a similar spectrum with peaks at about 4318, 4484, 4597, and 4660  $\text{cm}^{-1}$ . Bands at 4717 and 4481  $\text{cm}^{-1}$  in polybutadiene have been assigned as second overtones of the symmetric and asymmetric bending vibrations of the  $\text{CH}_2$  of the

**Table 3.1 Alkene Functional Groups**

| Functional Group   | CH Peak in $\text{cm}^{-1}$ | CH Peak in nm |
|--|-----------------------------|---------------|
| Vinyl (hexene) $\text{CH}_2=\text{CH}-$                          | 6120                        | 1635          |
| Vinylidene (3-chloro-2-methyl-1-propene) $\text{CH}_2=\text{C}<$ | 6130                        | 1631          |
| Vinyl on N (1-ethenyl 2-pyrrolidinone)                           | 6170                        | 1621          |
| Vinyl on O (1-ethenyloxybutane)                                  | 6200                        | 1613          |
| Vinyl and vinylidene (2-methyl-1,3-butadiene)                    | 6130/6140                   | 1631/1629     |
| Acrylate $\text{CH}_2=\text{CHCOO}^-$                            | 6169*                       | 1621*         |
| Alkyne (1-hexyne) $\text{HC}\equiv$                              | 6536                        | 1530          |

\* According to Gerasimov and Snaveley this peak is actually a combination of vibrations, one quantum of energy from each of the two C-H bonds of the vinyl group, and the actual first overtone is at  $5998\text{ cm}^{-1}$  (1667 nm).



**FIGURE 3.2** Cis and trans compounds, cis-3-hexene-1-ol (dotted curve) and trans-2-hexene-1-ol (solid). Note: Peaks specific to cis double bonds are indicated with arrows.

uncoupled vinyl group, as interpreted by a local mode model.<sup>3</sup> There are no corresponding fundamental vibrations for these peaks at  $1469$  and  $1572\text{ cm}^{-1}$ , though; only the overtones are observed. The overtones at  $2X$  and all other even multiples are not observable because they coincide with stronger CH stretching vibrations. The third vinyl peak, at  $4600\text{ cm}^{-1}$ , has also been attributed to a bending mode by Snaveley and Angevine,<sup>3</sup> as has the  $4717\text{ cm}^{-1}$  peak.

These vinyl bands have also been discussed by McManis and Gast.<sup>6</sup> The  $4482\text{ cm}^{-1}/2230\text{ nm}$  peak has been used to quantify the vinyl group, having an absorptivity of about  $0.87\text{ L/mole-cm}$ . The peak shifts slightly in allyl esters

and ethers, and splits into two peaks when a carbonyl is present. The  $4600\text{ cm}^{-1}/2170\text{ nm}$  peak was observed in all vinyl compounds except vinyl esters. Its absorptivity is about  $0.2\text{ L/mole-cm}$ . The  $4700\text{ cm}^{-1}/2100\text{ nm}$  peak has an absorptivity of about  $0.45\text{ L/mole-cm}$ .

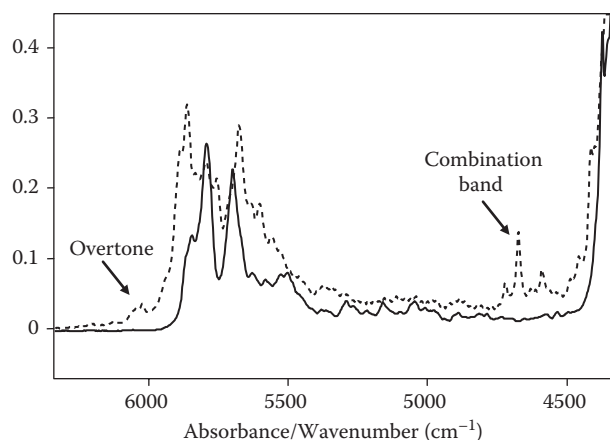
Higher-order overtones of the  $4481$  and  $4717\text{ cm}^{-1}$  peaks have also been noted at  $7346\text{ cm}^{-1}$  ( $1360\text{ nm}$ ) and  $7750\text{ cm}^{-1}$  ( $1290\text{ nm}$ ). The  $4600\text{ cm}^{-1}$  peak also shows a second member of a progression at  $7508\text{ cm}^{-1}$  ( $1332\text{ nm}$ ). Its absorptivity has been reported to be about  $0.01\text{ L/g-cm}$ .

As in the CH stretch overtones, trans double bonds do not have distinctive absorptions in the combination region, but cis double bonds do. There is a strong cis peak near  $4673\text{ cm}^{-1}$  ( $2140\text{ nm}$ ) that can be used for quantification and a second peak near  $4587\text{ cm}^{-1}$  ( $2180\text{ nm}$ ). These peaks are pointed out in Figure 3.2.

### 3.3 Cyclic Double Bonds

When cyclohexene is compared to cyclohexane, the most readily apparent difference occurs at the combination band near  $4670\text{ cm}^{-1}$  ( $2140\text{ nm}$ ), similar to the cis double bond in straight-chain alkenes. There are additional bands in the overtone area as well. A small doublet near  $6050\text{ cm}^{-1}$  ( $1650\text{ nm}$ ) might also be attributed directly to the CH stretch next to the double bond. See Figure 3.3.

Cyclopentene also has a distinct combination band near  $4660\text{ cm}^{-1}$  ( $2145\text{ nm}$ ) and four peaks near  $6000\text{ cm}^{-1}$  ( $1667\text{ nm}$ ) that are not present in cyclopentane. At



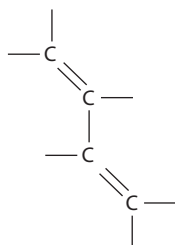
**FIGURE 3.3** Cyclohexane (solid curve) and cyclohexene (dotted).

8777  $\text{cm}^{-1}$  (1140 nm) there is a single, very distinctive CH second overtone due to the CH of the double bond.<sup>9</sup> Wong and associates have analyzed and discussed fifth overtone spectra of cyclic alkenes.<sup>10</sup>

The first overtone of the CH stretch of the double bond in norbornenes was determined to be in the range of 5970–6080  $\text{cm}^{-1}$  (1645–1675 nm).<sup>11</sup> The attribution of this absorption band to the CH groups next to the double bonds and not the bridgehead CH was confirmed by examination of model compounds that lacked the vinyl CHs and retained the bridgehead CH. The effect of a number of different substituents on the band position was also studied.

### 3.4 Dienes

Dienes are described by the following structure and comprise a set of molecules with somewhat unique properties.



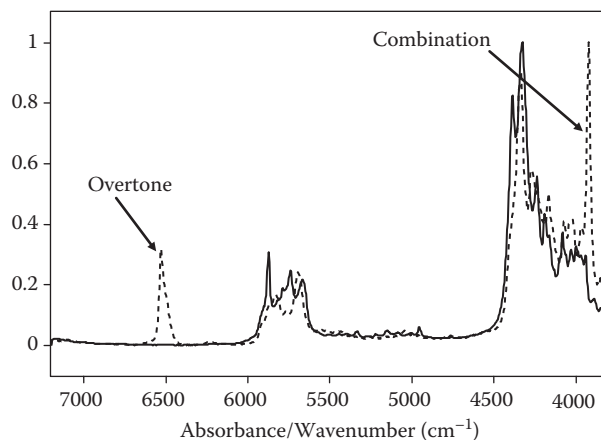
As in aromatic compounds, dienes demonstrate multiple bands associated with conjugated double-bond and C-H stretching. The mid-infrared spectra of conjugated

polyenes exhibit a band in the 1000 to 900  $\text{cm}^{-1}$  (10000 to 11111 nm) region, which does not have overtones or combination bands observed in the near infrared. This band is indicative of cis and trans groups within the different polyenes.<sup>12</sup> The near-infrared bands associated with  $\nu$  H-C=C are observed near 6110  $\text{cm}^{-1}$  (1637 nm), 5960  $\text{cm}^{-1}$  (1678 nm), 4710  $\text{cm}^{-1}$  (2123 nm), 4595  $\text{cm}^{-1}$  (2176 nm), and 4470  $\text{cm}^{-1}$  (2237 nm), and are very similar to those shown for 1-hexene in Figure 3.1. The  $3\nu$  C=C band is observed near 4950  $\text{cm}^{-1}$  (2020 nm). Note that the Appendix material provides more examples of model spectra as well as tables showing precise band positions.

### 3.5 Alkynes and Allenes

The CH stretch of a proton next to a triple bond occurs near 6500  $\text{cm}^{-1}$  (1538 nm), and is very distinctive and isolated from other CH absorption peaks. There is also a combination band at 3930  $\text{cm}^{-1}$  (2545 nm) that could be the sum of the CH stretch and the CH wag. These are shown in Figure 3.4. 2-Hexyne, which has no proton on its triple bond, is shown for comparison. A second overtone of the CH stretch occurs at about 9600  $\text{cm}^{-1}$  (1042 nm).

Allene,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ , is said to have its first CH overtone at 6139  $\text{cm}^{-1}$  (1629 nm) and a combination band at 6031  $\text{cm}^{-1}$  (1658 nm). Second and third overtones have been reported at 8620  $\text{cm}^{-1}$  and 11765  $\text{cm}^{-1}$  (1160 and 850 nm).<sup>8</sup>



**FIGURE 3.4** 1-hexyne (dotted curve) and 2-hexyne (solid).



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# Chapter 4

## **Aromatic Compounds**

## 4.1 Benzene

The near-infrared (NIR) spectrum of benzene has been thoroughly described by Kaye<sup>1</sup> and others. Benzene is such a highly symmetrical molecule that only a few of its vibrations are infrared active. However, the inactive modes participate in the overtones and combinations of the NIR. An explanation for the nomenclature of the fundamental vibrational modes used by Kaye is provided in Figure 4.1 from Avram and Mateescu.<sup>2</sup> Only the vibrations labeled “IR” have fundamental IR bands. The band assignments for the first combination and first overtone regions are provided in Table 4.1, using the Herzberg nomenclature as described in Figure 4.1.

The first overtone doublet near 6000  $\text{cm}^{-1}$  (1670 nm) is actually composed primarily of IR inactive CH stretching vibrations. As described in Table 4.1 and Figure 4.1,

both of the bands near 6000  $\text{cm}^{-1}$  are composed of a Raman active vibration and a vibration that is somewhat IR and Raman active ( $\nu_{12}$ ). Note the Benzene spectrum in Figure 4.2.

The second overtone peak at 8834  $\text{cm}^{-1}$  (1132 nm) represents the second overtone of the infrared active CH stretch (vibration 12 in Herzberg notation and Figure 4.1).<sup>3</sup> A nearby peak at 8770  $\text{cm}^{-1}$  (1140 nm) has been assigned as a combination of twice the CH stretch plus either 14 and 19 or 8 and 9. A third overtone is at 11442  $\text{cm}^{-1}$  (874 nm) neat, and 11364  $\text{cm}^{-1}$  (880 nm) in carbon tetrachloride. The fourth overtone is at about 14000  $\text{cm}^{-1}$  (714 nm).

The strong peak at 4050  $\text{cm}^{-1}$  (2469 nm) is therefore a combination of vibrations 14 and 15 of Figure 4.1, a CH stretch, and CH bending as described in the figure. The series of absorptions near 4660  $\text{cm}^{-1}$  (2146 nm) combine CC stretching with CH stretching. Combination peaks near

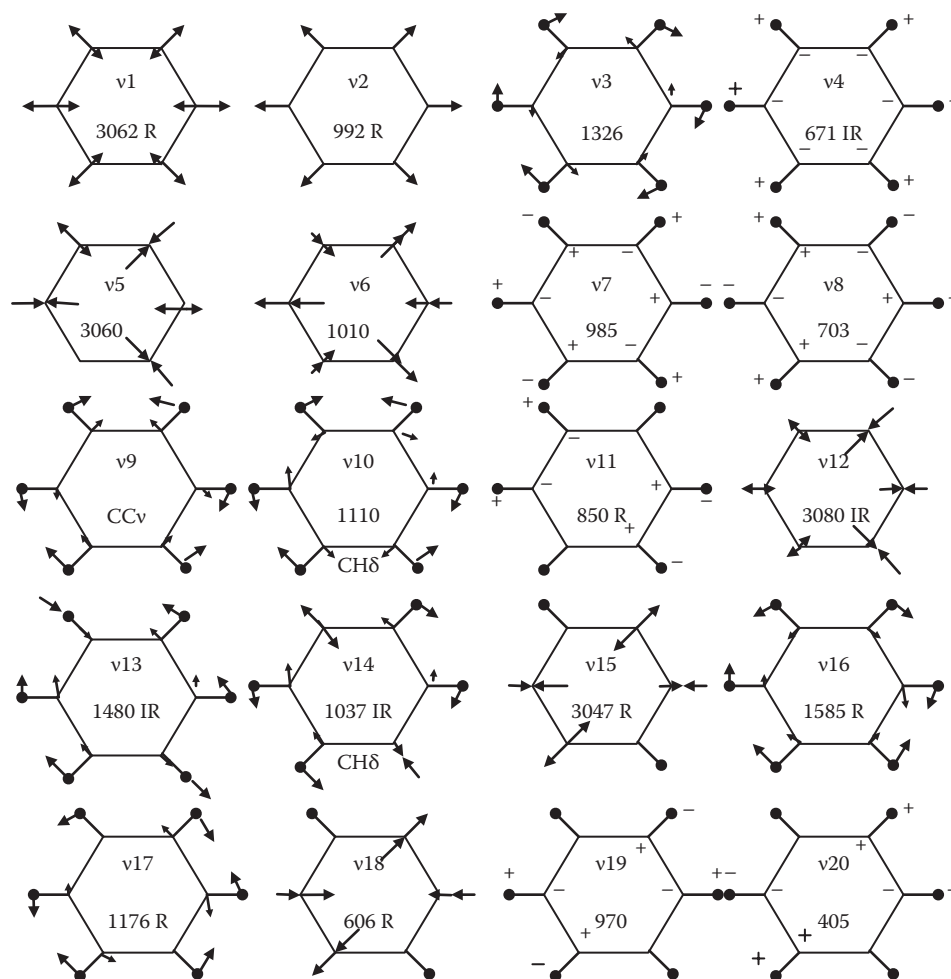
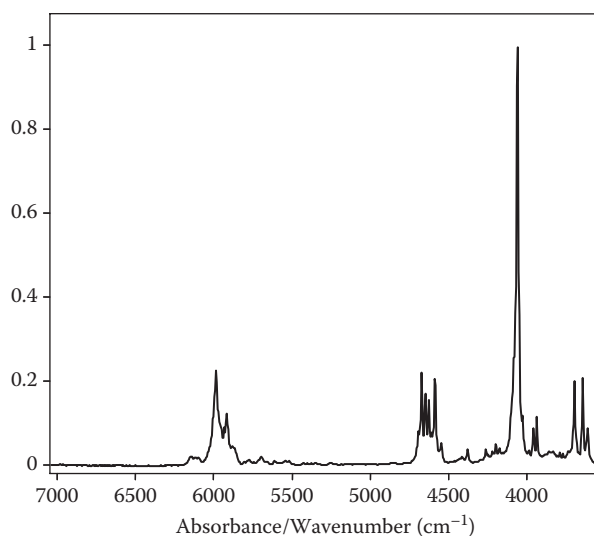


FIGURE 4.1 Herzberg symbols.

**Table 4.1 Benzene Band Assignments**

| Assignment | Vibrations            | Calculated Wavenumber | Observed Wavenumber | Observed Wavelength (nm) |
|------------|-----------------------|-----------------------|---------------------|--------------------------|
| 18 + 5     | CC $\delta$ +CH $\nu$ | 3666                  | 3613 (3613)         | 2768                     |
| 12 + 18    | CH $\nu$ +CC $\delta$ | 3705                  | 3640 (3643)         | 2747                     |
| 8 + 5      | CC $\omega$ +CH $\nu$ | 3731                  | 3693 (3697)         | 2708                     |
| 4 + 1      | CH $\omega$ +CH $\nu$ | 3733                  | Masked              | —                        |
| 7 + 5      | CC $\omega$ +CH $\nu$ | 3763                  | 3722 (3735)         | 2687                     |
| 11+ 12     | CC $\omega$ +CH $\nu$ | 3948                  | 3937 (3935)         | 2540                     |
| 19 + 15    | CC $\omega$ +CH $\nu$ | 4017                  | 3960 (3958)         | 2525                     |
| 15 + 6     | CH $\nu$ +CC $\delta$ | 4047                  | 3980 (3986)         | 2513                     |
| 14 + 15    | CC $\delta$ +CH $\nu$ | 4084                  | 4050 (4060)         | 2469                     |
| 12 + 2     | CH $\nu$ +CC $\nu$    | 4091                  | Shoulder            | —                        |
| 14 + 1     | CC $\delta$ +CH $\nu$ | 4099                  | Shoulder            | —                        |
| 15 + 10    | CH $\nu$ +CH $\delta$ | 4157                  | 4155 (4175)         | 2407                     |
| 17 + 5     | CC $\delta$ +CH $\nu$ | 4238                  | 4190 (4198)         | 2387                     |
| 12 + 17    | CH $\nu$ +CH $\delta$ | 4277                  | 4252 (4263)         | 2352                     |
| 12 + 3     | CH $\nu$ +CH $\delta$ | 4425                  | 4360 (4379)         | 2294                     |
| 13 + 15    | CC $\nu$ +CH $\nu$    | 4532                  | 4532 (4549)         | 2206                     |
| 13 + 1     | CC $\nu$ +CH $\nu$    | 4547                  | 4570 (4584)         | 2188                     |
| 16 + 5     | CC $\nu$ +CH $\nu$    | 4656                  | 4615 (4625)         | 2167                     |
| 12 + 16    | CH $\nu$ +CC $\nu$    | 4695                  | 4642 (4644)         | 2154                     |
| 15 + 9     | CH $\nu$ +CC $\nu$    | 4695                  | 4655 (4675)         | 2148                     |
| 15 + 5     | CH $\nu$ +CH $\nu$    | 6107                  | 5920 (5914)         | 1689                     |
| 12 + 1     | CH $\nu$ +CH $\nu$    | 6161                  | 5985 (5988)         | 1671                     |

*Note:* The wavenumbers in parentheses represent peak positions determined by the author.

**FIGURE 4.2** Spectrum of benzene.

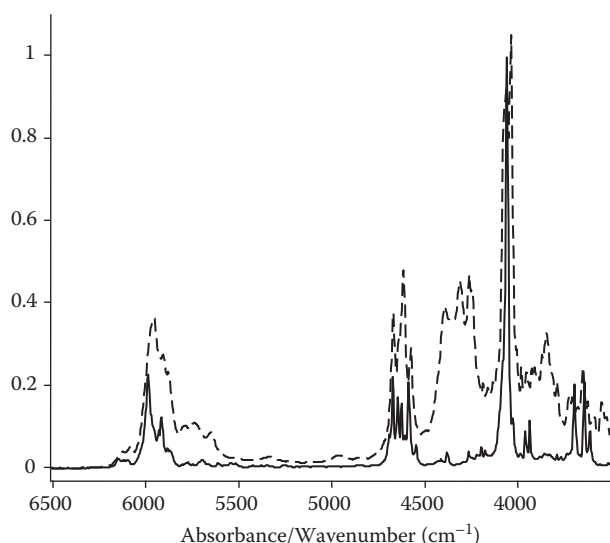
3640  $\text{cm}^{-1}$  (2747 nm) are CH stretching combined with CC or CH wagging vibrations.

Deuterated benzene ( $\text{C}_6\text{D}_6$ ) has bands at 1900, 1560, 1375, and 1010 nm, which correspond to the first, second, third, and fourth overtone of C-D stretching, respectively.<sup>1</sup>

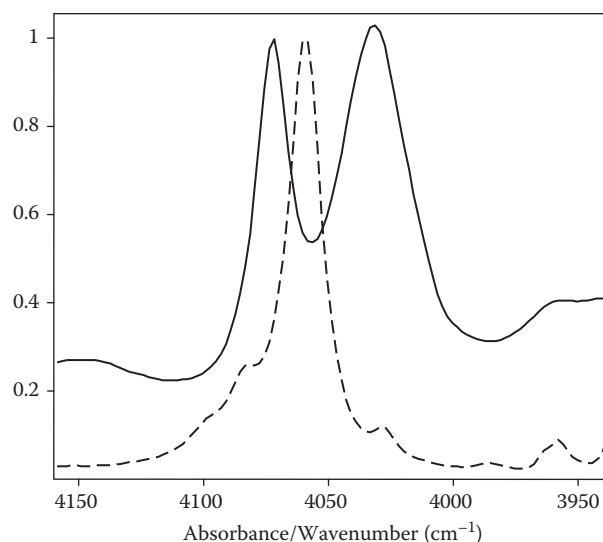
## 4.2 Substituted Aromatics: Alkyl

Substitution on the benzene ring reduces the symmetry of the molecule, potentially allowing for additional vibrational peaks. In the case of alkyl aromatics, there is also the addition of the alkyl absorptions. Figure 4.3 compares the near-infrared spectra of benzene and toluene. The primary differences appear to be the addition of the methyl combination bands near 4300  $\text{cm}^{-1}$  (2300 nm) and the methyl first overtones near 5800  $\text{cm}^{-1}$  (1750 nm). There is also a noticeable peak at 3836 nm (2607 nm) that could be related to the sum of a CH stretch and one of the ring wagging vibrations involving a ring with five adjacent protons.

Alkyl groups on the benzene ring displace the CH overtone band to a lower wavenumber (longer wavelength) due to their electropositive nature. Also, as seen in Figure 4.4, the strong peak in the region of 4060  $\text{cm}^{-1}$  (2460 nm) is a doublet in mono-, di-, and tri-substituted methylbenzenes. The lower wavenumber peak in this doublet has been attributed to the CH stretch/CC bending mode previously described, whereas the peak near 4080  $\text{cm}^{-1}$  (2452 nm) has been assigned as the second overtone of the symmetric



**FIGURE 4.3** Comparison of benzene (solid curve) and toluene (dotted curve).



**FIGURE 4.4** Comparison of benzene (dotted curve) and m-xylene (solid curve) in the 4100  $\text{cm}^{-1}$  region.

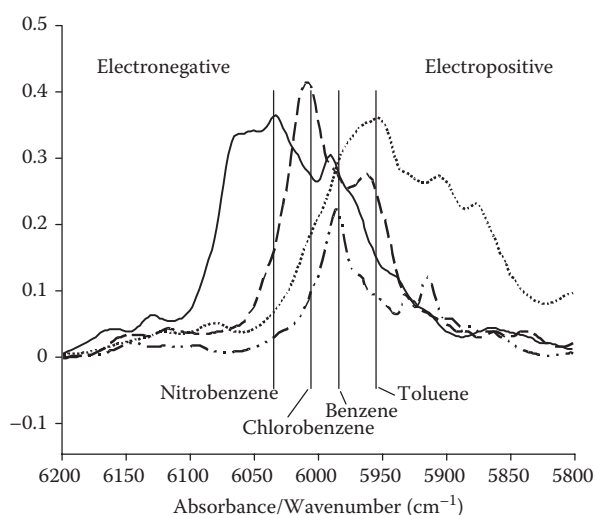
methyl bending vibration.<sup>4</sup> A linear relationship was found between the number of methyl groups substituted on the benzene ring and the intensity of this characteristic absorption band. The 4080  $\text{cm}^{-1}$  band gave a good measure for aromatic compounds with 1-4 methyl groups. In higher substituted methylbenzenes, such as durene and pentamethylbenzene, the first overtone band at 5660  $\text{cm}^{-1}$  (1767 nm) provides better predictions.

With regard to higher vibrational states, the second overtone of the aromatic CH stretch in alkylated benzenes occurs at 8734  $\text{cm}^{-1}$  (1145 nm), whereas the alkyl CH stretch occurs at 8389  $\text{cm}^{-1}$  (1192 nm). Approximately 5 to 10 nm shifts were observed to lower frequency (longer wavelength) as compared with benzene's second CH overtone band.

## 4.3 Substituted Aromatics: Nonalkyl

As shown in Figure 4.5, electronegative groups, such as halogens or nitro groups, produce shifts to higher wavenumber (lower wavelength), and electropositive substituents (alkyl group) generate a displacement to lower wavenumber.

In an investigation of NIR absorptions using photoacoustic experiments, the tentative assignments of 11 substituted benzenes have been reported.<sup>5</sup> These included three benzonitriles, five acetophenones, and three benzylbromides. An example of a typical band assignment for 2,2,4-trichloroacetophenone given in this work is:

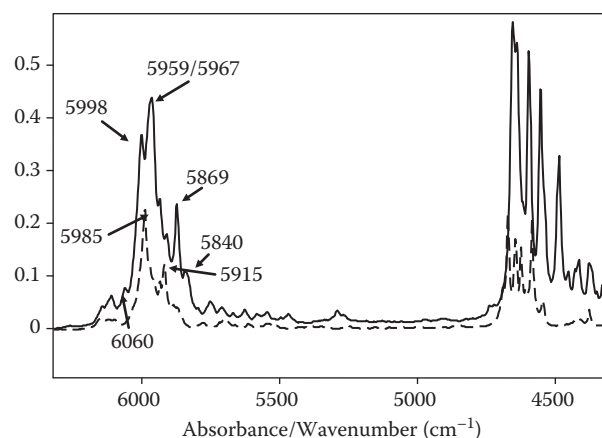


**FIGURE 4.5** First overtone peak shifting with electronegativity of substituents on benzene ring. (From Weyer, L. G., Lo, S.-C., *Spectra-Structure Correlations in the Near-infrared Vol. 3*, pp. 1817–1837 in *Handbook of Vibrational Spectroscopy*, Chalmers, J. C. and Griffiths, P. R., Eds., John Wiley & Sons, 2002. With permission).

|                                 |   |
|---------------------------------|---|
| 4057 cm <sup>-1</sup> (2465 nm) | – Sum of 2927 and 1070 cm <sup>-1</sup>         |
| 4141 cm <sup>-1</sup> (2415 nm) | – Sum of 3100 and 1070 cm <sup>-1</sup>         |
| 4246 cm <sup>-1</sup> (2355 nm) | – Sum of 3100 and 1162 cm <sup>-1</sup>         |
| 4320 cm <sup>-1</sup> (2315 nm) | – Sum of 2950 and 1406 cm <sup>-1</sup>         |
| 4494 cm <sup>-1</sup> (2225 nm) | – Sum of 2950 and 1479 cm <sup>-1</sup>         |
| 4651 cm <sup>-1</sup> (2150 nm) | – Sum of 3100 and 1590 cm <sup>-1</sup>         |
| 4938 cm <sup>-1</sup> (2025 nm) | – Sum of 2998/2950 and 2 × 991 cm <sup>-1</sup> |
| 5141 cm <sup>-1</sup> (1945 nm) | – 3 × 1716 cm <sup>-1</sup>                     |
| 5291 cm <sup>-1</sup> (1890 nm) | – Sum of 3100 and 2 × 1070 cm <sup>-1</sup>     |
| 5540 cm <sup>-1</sup> (1805 nm) | – Sum of 2950 and 2 × 1282 cm <sup>-1</sup>     |
| 5731 cm <sup>-1</sup> (1745 nm) | – 2 × 2858 cm <sup>-1</sup>                     |
| 5935 cm <sup>-1</sup> (1685 nm) | – 2 × 2950 cm <sup>-1</sup>                     |
| 6173 cm <sup>-1</sup> (1620 nm) | – 2 × 3100 cm <sup>-1</sup>                     |
| 6431 cm <sup>-1</sup> (1555 nm) | – Sum of 2998 and 2 × 1708 cm <sup>-1</sup>     |
| 6667 cm <sup>-1</sup> (1500 nm) | – 2 × 2950 plus 727 cm <sup>-1</sup>            |
| 6897 cm <sup>-1</sup> (1450 nm) | – 2 × 2950 plus 991 cm <sup>-1</sup>            |
| 7273 cm <sup>-1</sup> (1375 nm) | – 2 × 2998 plus 1282 cm <sup>-1</sup>           |
| 7752 cm <sup>-1</sup> (1290 nm) | – 2 × 2998 plus 1708 cm <sup>-1</sup>           |
| 8230 cm <sup>-1</sup> (1215 nm) | – 3100 plus 3 × 1708 cm <sup>-1</sup>           |
| 8969 cm <sup>-1</sup> (1115 nm) | – 3 × 2950/2998 cm <sup>-1</sup>                |

## 4.4 Other Aromatic Compounds

The presence of a heteroatom in an aromatic ring splits the CH overtone peaks rather than shifting them. For



**FIGURE 4.6** Comparison of benzene (dashed) and pyridine (solid) spectra.

example, in liquid pyridine there is a doublet at each overtone with the lower energy peak attributed to the CH stretching absorptions of the 2 and 6 positions, and the higher energy peak due to the 3, 4, and 5 positions.<sup>6</sup> This is shown in Figure 4.6. These peaks appear at 5835 and 5867 cm<sup>-1</sup> (1714 and 1704 nm) for the 2,6-positions, and 5907 and 5956 cm<sup>-1</sup> (1693 and 1679 nm) for 3, 4, and 5 positions. Bini et al. suggest that the 3, 4, and 5 position peaks appear as only one peak due to overlap.<sup>7</sup>

The highest wavenumber peak in the region near 6000 cm<sup>-1</sup> has been assigned by Bini et al. as a combination of two CH stretching vibrations both involving the 2,6-positions. The smaller peaks at 6060, 6105, and 6139 cm<sup>-1</sup> are also combinations of 2,6 and 3,5; 3,5 and 3,5; and 3,5 and 3,5 stretching vibrations.

Figure 4.6 also shows the first combination spectral region of benzene and pyridine near 4500–4700 cm<sup>-1</sup>. The distinctive set of four large peaks and several smaller ones are considerably shifted for pyridine, relative to benzene. The assignments for these peaks are given in Table 4.1. All are combinations involving a CH stretch and another vibration.

Thiophene, furan, and pyrrole also have two peaks at each overtone.<sup>6</sup> The spectra of gases of these compounds all shift to higher energy (lower wavelength), relative to the spectra of liquids.

The second overtones of CH stretch peaks for liquid pyridine occur at 8785 cm<sup>-1</sup> (1138 nm) and 8651 cm<sup>-1</sup> (1156 nm). The third and fourth overtones are at 11296 and 11474 cm<sup>-1</sup> (885 and 872 nm), and 13810 and 14037 cm<sup>-1</sup> (724 and 712 nm), respectively. The lower frequency band

has been assigned to CH stretches at the 2 and 6 positions and the higher frequency band was attributed to the CH stretches at the 3, 4, and 5 positions.

In a study of methyl-substituted pyridines, the aryl regions of the overtones show a simplified structure having one peak progression for each nonequivalent CH. The methyl regions of the methylpyridines show complex profiles. The band profile in 3- and 4-methylpyridine is similar to that of toluene since the methyl groups of these compounds are free rotors and all have a low energy barrier to rotation. However, the methyl band profiles of 2-methylpyridine are complex, and these patterns indicate that vibration-torsional coupling is an important contributor to the complex structure.<sup>8</sup>

The near-infrared spectrum of the five-membered ring aromatic organometallic compound ferrocene has also been examined.<sup>9</sup> The CH stretch first overtone of the mid-IR 3080  $\text{cm}^{-1}$  peak occurs at 6105  $\text{cm}^{-1}$  (1638 nm). A combination peak at 4495  $\text{cm}^{-1}$  (2225 nm) has been assigned as a combination of the 1400  $\text{cm}^{-1}$  C-C stretch mid-IR peak and the CH stretch. A doublet centered at 4167  $\text{cm}^{-1}$  (2400 nm) appears to be due to combination of the asymmetric and symmetric ring-breathing vibrations (1000 and 1100  $\text{cm}^{-1}$  in the mid-IR) with CH stretching. And a strong peak at 3945  $\text{cm}^{-1}$  (2535 nm) is a combination of the 810  $\text{cm}^{-1}$  CH bending with the 3080  $\text{cm}^{-1}$  CH stretch. Lewis also suggested that two smaller peaks observed at 4367  $\text{cm}^{-1}$  (2290 nm) and a broad peak near 4800  $\text{cm}^{-1}$  (2083 nm) are combinations of the CH stretch with two inactive IR bands at 1257  $\text{cm}^{-1}$  (CH bend) and 1560  $\text{cm}^{-1}$  (C-C stretch), respectively.

Heterocyclic aromatics with a prominent N-H band include pyrrole and indole where the nitrogen is attached

to a single hydrogen. For these compounds the strong first overtone N-H is apparent at 6835  $\text{cm}^{-1}$  (1463 nm), and the combination band is observed at 4715  $\text{cm}^{-1}$  (2121 nm). The N-H overtone can be shifted by as many as 400  $\text{cm}^{-1}$  when other substituents are present, such as in 2,2-dimethyl-thiazolidine where the band is observed near 6450  $\text{cm}^{-1}$  (1550 nm). When N-H is present in the heterocyclic compound, a second overtone bending band may be observed as a very weak shoulder near the 4715  $\text{cm}^{-1}$  (2121 nm) position. Other differences between heterocyclics are found in the C-H region between 6300  $\text{cm}^{-1}$  to 5700  $\text{cm}^{-1}$  (1587 nm to 1754 nm).

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# Chapter 5

## **Hydroxyl-Containing Compounds**

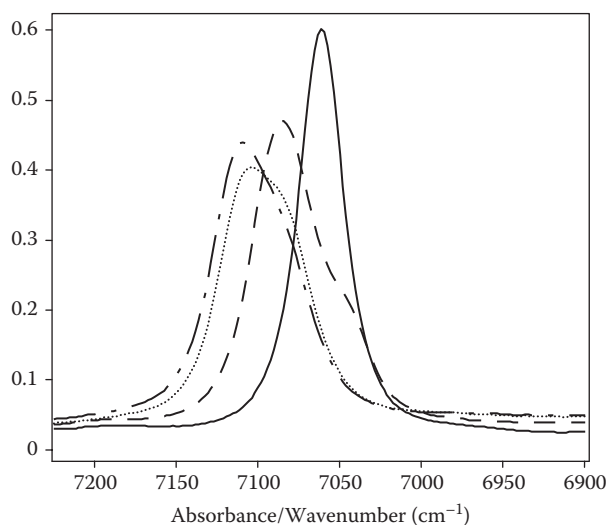
## 5.1 O-H Functional Groups

The hydroxyl group has been extensively studied in the near-infrared (NIR) region, particularly with respect to hydrogen bonding. The advantages of longer pathlength cells for liquids and direct analysis of solids have contributed to the utility of NIR for hydrogen-bonding studies in a great variety of mixtures and environments. Also, NIR offers a special advantage over the mid-IR in the measurement of mixtures of water and other hydroxyl-containing compounds because the combination peaks of water and other hydroxyls are well separated from one another in NIR.

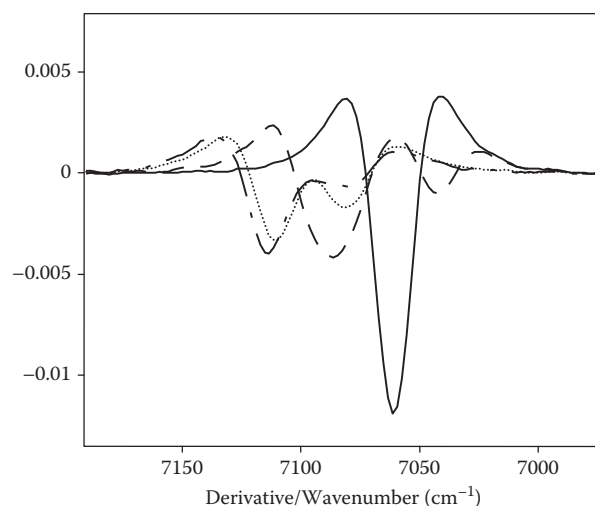
## 5.2 O-H in Alcohols

### 5.2.1 Alcohols, First Overtone Region

The first overtone of a free hydroxyl group in dilute  $\text{CCl}_4$  solution or a low-density gas is at about  $7090\text{ cm}^{-1}$  ( $1410\text{ nm}$ ). This peak is at different positions for primary, secondary, and tertiary alcohols, as seen in Figure 5.1. Primary and secondary butanols can be split into doublets by rotational isomerization.<sup>1</sup> The splits are better seen



**FIGURE 5.1** First overtone of OH peak in butanols. Notes: The dot-dashed curve is isobutanol (a primary alcohol), the dotted curve is 1-butanol, the dashed curve is sec-butanol, and the solid curve is *tert*-butanol. (From Weyer, L. G., Lo, S.-C., *Spectra-Structure Correlations in the Near Infrared* pp. 1817–1837, Vol. 3 in *Handbook of Vibrational Spectroscopy*, Chalmers, J. C., Griffiths, P. R., Eds., John Wiley & Sons, New York, 2002. With permission.)

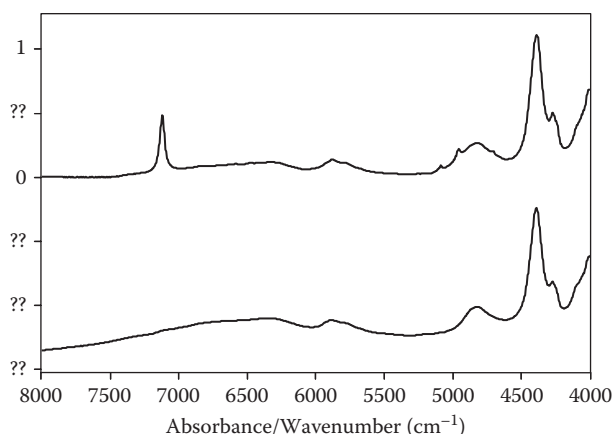


**FIGURE 5.2** Derivative spectra of butanols.

in Figure 5.2, the second derivation spectra of the same spectral region. Czarnecki et al.<sup>1</sup> observed an additional peak in the first overtone region when they subtracted the spectrum at a lower temperature from that at a higher one. They felt that temperature effects further separated species that were weakly bonded to the carbon tetrachloride solvent and a terminal free OH of a self-associated species. A hydroxyl first overtone peak may also be split due to interactions with the electrons of phenyl rings or halogens, as in benzyl alcohol, for example.

In hydrogen-bonded alcohols, there is a broad peak in the  $1460\text{--}1600\text{ nm}$  region ( $6850\text{ cm}^{-1}$  to  $6240\text{ cm}^{-1}$ ), which has been generally attributed to the first overtone of the hydroxyl. This bonded OH peak appears to be broader as a first overtone than its fundamental, as was observed in a series of spectra taken at different temperatures.<sup>2</sup> On the other hand, the nonbonded OH first overtone is stronger relative to the bonded species than it is in the fundamental and can be readily detected even when not visible in the fundamental region.<sup>3</sup> Figure 5.3 illustrates the differences between the bonded and nonbonded hydroxyls of methanol. The broad-bonded OH is indistinct, whereas the nonbonded OH in a dilute carbon tetrachloride solution is very sharp and strong.

Temperature and concentration-dependent variations in self-association of 1-octanol have also been studied by two-dimensional (2D) Fourier transform near IR correlation spectroscopy.<sup>4</sup> The population of the free OH groups increases with temperature, reportedly reaching 13% at  $80^\circ\text{C}$ . The molar absorptivities of the first and second overtones of the monomer were found to be similar



**FIGURE 5.3** Methanol in  $\text{CCl}_4$  (top) and neat (bottom) spectra.

in several nonhydrogen bonding solvents such as carbon tetrachloride, heptane, and octane. The first overtone's absorptivity was about 1.7 L/mole-cm, which agrees with Goddu's data.<sup>5</sup> The absorptivity of the second overtone is about 1/20 that of the first.

Hydrogen bonding of alcohols occurs to different extents with solvents with varying bonding strengths. The spectra of methanol in a series of solvents from carbon tetrachloride through pyridine have been studied.<sup>6,7</sup> The first overtone region exhibits two major bonded OH peaks near 6800 and 7100  $\text{cm}^{-1}$  (14700 and 1280 nm) when an alcohol is in a solvent capable of hydrogen bonding. Bell and Barrow<sup>6</sup> have shown that the ratio of these two peaks is not affected by temperature or dilution (except for the formation of dimer at very high concentrations). They also show that the second peak is not due to an OH-CH combination band. They suggest that the two peaks are both monomeric hydrogen-bonded alcohol first overtones and that the vibrational energy level has been split into two, creating a double minimum in the potential energy curve.

### 5.2.2 Higher-Order Overtones

The second overtone of the nonbonded OH stretch occurs at about 10400  $\text{cm}^{-1}$  (960 nm) and the third at about 13500  $\text{cm}^{-1}$  (740 nm) for simple alcohols. The second overtone has also been used for a number of hydrogen bonding studies.<sup>8</sup> Variations in the structure of the alcohol result in splitting of the band and systematic shifts. Second overtones of OH stretch appear to have less interference from CH combination bands than first overtones and can therefore be more useful for thermodynamic studies.<sup>7</sup>

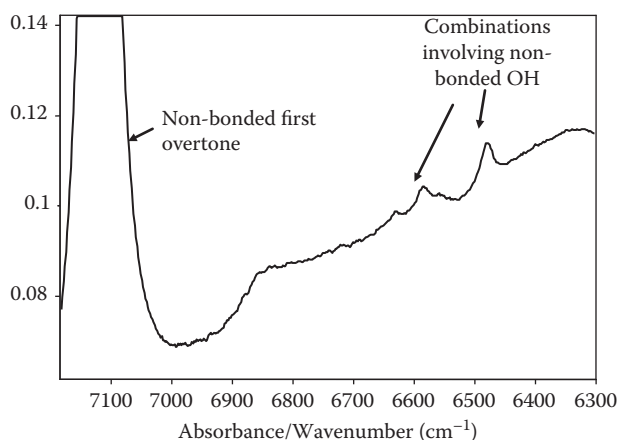
Additional overtones of the nonbonded hydroxyl stretch of alcohols, using gaseous ethanol as a model, are the fourth at 16700  $\text{cm}^{-1}$  (600 nm) and the fifth at 19500  $\text{cm}^{-1}$  (510 nm).<sup>9</sup> Additional bonded hydroxyl bands include the OH stretch second overtone at 9550  $\text{cm}^{-1}$  (1047 nm), a combination of the first overtone of the OH stretch and twice the methyl CH deformation at 9386  $\text{cm}^{-1}$  (1065 nm), and a combination of the OH stretch first overtone plus three times the CO stretch at 9720  $\text{cm}^{-1}$  (1029 nm).<sup>10</sup>

### 5.2.3 Combination Bands

A distinctive combination region of alcohols occurs between 4550 and 5550  $\text{cm}^{-1}$  (1800–2200 nm). This broad peak, a combination of OH stretching and OH bending, has been used in a large number of quantitative analyses including hydroxyl number of polymers, alcohols in the presence of water, and ethylene vinyl alcohol content in copolymers. As shown in Figure 5.3, it is present to some extent in both dilute solution and neat spectra of hydroxyl-containing compounds.

In the dilute solution spectrum of methanol, three sharp peaks are observed superimposed on the broader continuum. These can be seen clearly in Figure 5.3. The sharp peaks have been assigned to OH stretch plus CH bending at 5090  $\text{cm}^{-1}$  (1965 nm), OH stretch plus OH bending at 4960  $\text{cm}^{-1}$  (2017 nm), and OH stretch plus CO stretch at 4710  $\text{cm}^{-1}$  (2124 nm).<sup>11</sup> There is also a second combination of OH stretching and a different OH bending mode at about 3970  $\text{cm}^{-1}$  (2520 nm). These sharp peaks are at different positions in other alcohols. In the neat spectrum, these peaks are seen as only one broad band centered at about 4770  $\text{cm}^{-1}$  (2100 nm). In the mid-IR, a diffuse OH association band related to deformation occurs at about 1420  $\text{cm}^{-1}$ , which can account for the 4770  $\text{cm}^{-1}$  NIR band ( $1420 \text{ cm}^{-1} + 3350 \text{ cm}^{-1} = 4770 \text{ cm}^{-1}$ ). The diffuse mid-IR band is said to disappear in dilute solutions of alcohols, where hydrogen bonding does not occur.<sup>12</sup> However, the broad combination peak does not disappear completely in the NIR.

There has been some confusion over whether combinations of OH stretch and CH stretch in the 6330  $\text{cm}^{-1}$  (1580 nm) region contribute to the broad hydrogen-bonded OH overtone peak.<sup>11,13</sup> Although Kaye<sup>11</sup> appears to assign the 6330  $\text{cm}^{-1}$  peak to this combination, he also says that combination bands involving CH stretch and OH stretch are very weak because stretching vibrations involving different atoms do not couple well unless their



**FIGURE 5.4** OH combination peaks near the much larger first overtone peak.

frequencies are nearly the same or the groups involve double bonds or rings. Kaye's apparent assignment may be simply a function of how one reads his chart, as the two small OH-CH peaks that are observable in his dilute  $\text{CCl}_4$  spectrum overlap the broad, bonded OH stretch first overtone. Figure 5.4 shows the small peaks near the much larger first overtone peak. Bell and Barrow<sup>6</sup> show that the small peaks (one in ethanol and two in methanol, due to coupling with asymmetric and symmetric CH stretch) are not present in  $\text{CD}_3\text{OH}$  dissolved in carbon tetrachloride. Czarnecki et al.<sup>14</sup> suggest that the series of peaks between  $6240\text{ cm}^{-1}$  ( $1600\text{ nm}$ ) and  $7100\text{ cm}^{-1}$  ( $1410\text{ nm}$ ) are all due to OH stretch first overtones of different aggregates, such as monomer, dimers, and polymers of the alcohols, but Czarnecki also says in a later article that a band at  $6500\text{ cm}^{-1}$  is a CH stretch and non-bonded OH stretch combination.<sup>4</sup> Czarnecki et al. found that the  $6330\text{ cm}^{-1}$  peak decreases with temperature when the monomeric  $7100\text{ cm}^{-1}$  peak increases, which supports their theory that it is due primarily to OH overtones. There are apparently contributions from both hydroxyl overtones and CH-OH combinations involved in the broad envelope, although the bonded OH first overtone probably predominates. The evidence of Davies and Rutland<sup>13</sup> does not contradict this statement.

There has also been a suggestion that a  $6319\text{ cm}^{-1}$  ( $1580\text{ nm}$ ) broad peak in ethylene-vinyl alcohol copolymers is due to a combination of OH stretching and 2 OH bending.<sup>15</sup> However, this peak is generally considered another hydrogen-bonded OH first overtone. See Figure 5.6 for a comparison.

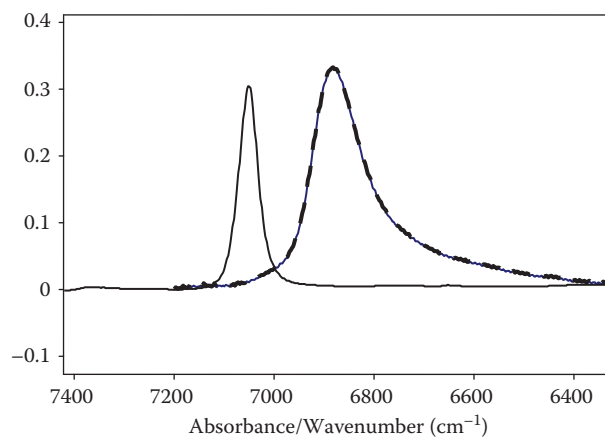
Higher wavenumber combination bands include one that combines the first overtone of the OH stretch and twice the methyl CH deformation at  $9386\text{ cm}^{-1}$  ( $1065\text{ nm}$ ), and a combination of the OH stretch first overtone plus three times the CO stretch at  $9720\text{ cm}^{-1}$  ( $1029\text{ nm}$ ).<sup>16</sup>

## 5.3 Phenols

### 5.3.1 Phenols: Overtones

Phenols show absorptions in the same regions as aliphatic alcohols, with first overtones near  $6940\text{--}7140\text{ cm}^{-1}$  ( $1400\text{--}1440\text{ nm}$ ). As seen in Figure 5.5, the first overtone of monomeric phenol in  $\text{CCl}_4$  is a single peak at  $7040\text{ cm}^{-1}$  ( $1420\text{ nm}$ ). Ortho-halogens can show a doublet due to cis/trans isomerism where the cis form is stabilized by internal hydrogen bonding between the hydroxyl and the halogen.<sup>17,18</sup> The cis form, represented by the large peak shown in Figure 5.5, is shifted to about  $6830\text{ cm}^{-1}$  ( $1464\text{ nm}$ ). The smaller trans peak is barely discernable in the figure. According to Wheeler, the ratio of the cis and trans peaks at different temperatures provides a measure of the stabilizing energy of the cis form.

The second overtone of dilute phenol in carbon tetrachloride is at  $10000\text{ cm}^{-1}$  ( $1000\text{ nm}$ ) and the third at  $13250\text{ cm}^{-1}$  ( $750\text{ nm}$ ). The second and third overtones of the o-halogenated phenols are doublets due to cis/trans configurations. For o-iodophenol, for example, the second overtone peaks are at  $9910$  and  $10290\text{ cm}^{-1}$  ( $1009$  and  $972\text{ nm}$ ) and the third overtones at  $12788$  and  $13400\text{ cm}^{-1}$  ( $782$  and  $746\text{ nm}$ ).



**FIGURE 5.5** First overtone of phenol in  $\text{CCl}_4$  (solid curve) and neat orthochlorophenol (dashed).

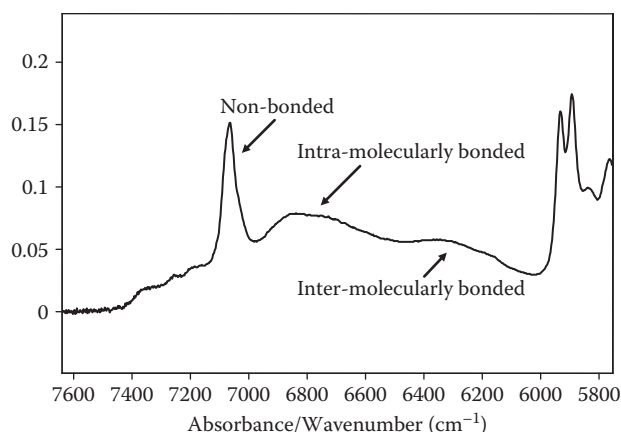
Due to the difference in acidity of phenol relative to simple aliphatic alcohols, its spectra in different solvents are quite different from those of methanol and ethanol.<sup>6</sup> In solvents of low hydrogen bonding capability, phenol shows both free and bonded OH first overtones because the solvent cannot bond the phenol completely. In solvents that are more capable of hydrogen bonding, phenol behaves like the alcohols, except that the sequence is accelerated. For example, the spectrum of phenol in N,N-dimethylformamide appears similar to the spectrum of ethanol in pyridine.

### 5.3.2 Phenols Combinations

In a study of combination bands of various halogenated phenols, Wulf et al.<sup>17</sup> found that most of the combinations involved the OH and bending or twisting modes of the aromatic ring or the OH group itself. This conclusion was based on the observation that pentachloro phenol, which had no CH groups, showed very similar patterns to the other model species. Rospenk et al.<sup>18</sup> compared the spectra of phenol and phenol-OD to show that a series of strong combination bands between 5210  $\text{cm}^{-1}$  (1920 nm) and 4760  $\text{cm}^{-1}$  (2100 nm) all involve the hydroxyl group, but no CH. The 5210  $\text{cm}^{-1}$  and 5080  $\text{cm}^{-1}$  peaks were assigned to OH stretch plus interactions with the ring, the 4949  $\text{cm}^{-1}$  to OH stretch plus OH deformation, and the 4867  $\text{cm}^{-1}$  and 4783  $\text{cm}^{-1}$  probably due to OH stretch plus C-O stretches with some interactions with other vibrations.<sup>16</sup>

## 5.4 Multiple Hydroxyl Compounds

Glycols and other compounds having more than one hydroxyl have the opportunity for different types of hydrogen bonding. These include many natural compounds such as sucrose, starch, and cellulose. Even in dilute solution, a diol will show an intramolecularly hydrogen-bonded hydroxyl peak.<sup>19</sup> Both bonded and nonbonded peaks are observed. The spectrum of 2-methyl-2,4-pentanediol in Figure 5.6 shows a nonbonded peak at 7065  $\text{cm}^{-1}$  (1415 nm) and an intramolecularly bonded peak at about 6850 (1460 nm). A small 6370  $\text{cm}^{-1}$  (1570 nm) intermolecularly bonded peak also appears. Based on information from the fundamental region, it is likely that the spacing between the nonbonded and the intramolecularly bonded peaks increases with the number of carbon atoms between the two hydroxyls.<sup>5,19</sup> Diols exhibit faster thermal



**FIGURE 5.6** Spectrum of 2-methyl-2,4-pentanediol showing how glycols and other compounds having more than one hydroxyl have the opportunity for different types of hydrogen bonding.

breaking of associates in the presence of water in dilute  $\text{CCl}_4$  than simple alcohols do.<sup>20</sup>

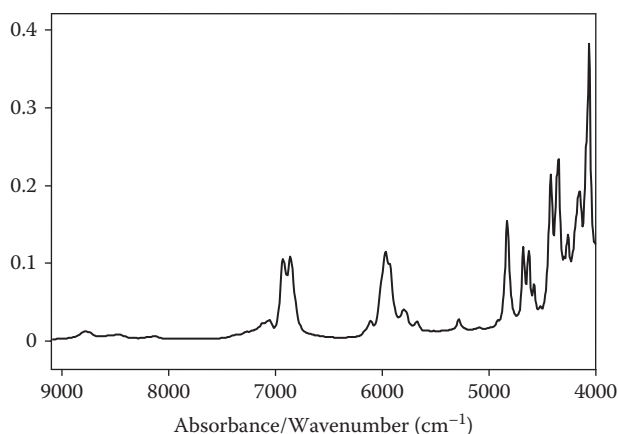
Carbohydrates in general may have a free OH stretch absorption near 6940  $\text{cm}^{-1}$  (1440 nm). This band has been reported in crystalline sucrose, for example, and has been assigned specifically to the C<sub>4</sub> hydroxyl within a crystalline matrix.<sup>21</sup> Trott et al.<sup>22</sup> discuss four different OH first overtone bands in carbohydrates in different solvent systems, using a monomer (glucose) and its polymer (glycogen) as models.

## 5.5 Hydroperoxides

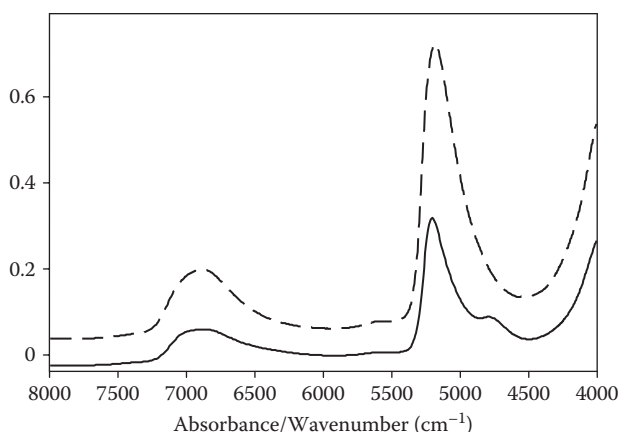
The first overtone of the nonbonded hydroxyl peak of a hydroperoxide in dilute solution is far enough removed from that of acids and alcohols that it can be used for quantitative analysis.<sup>5</sup> The peak is at about 6850  $\text{cm}^{-1}$  (1460 nm) as compared to 7100  $\text{cm}^{-1}$  (1410 nm) for alcohols. The spectrum of cumene hydroperoxide shown in Figure 5.7 shows a splitting of the hydroxyl peak due to interaction with the benzene ring. This doublet changes to a singlet in methylene chloride. There is also a combination band that probably involves the OH stretch and OH bending at about 4850  $\text{cm}^{-1}$  (2060 nm), again in dilute solution. These two bands were found to be characteristic of hydrogen peroxides derived from oxidized fatty esters in dilute carbon tetrachloride solutions.<sup>23</sup>

Normally  $\text{H}_2\text{O}_2$  is available as a dilute solution in water, and its OH first overtone is hydrogen bonded and obscured by that of water. However, the combination band near





**FIGURE 5.7** Cumene hydroperoxide.



**FIGURE 5.8** Hydrogen peroxide solution (solid curve) compared to water (dashed curve).

4850  $\text{cm}^{-1}$  (2060 nm) can be clearly observed, as shown in Figure 5.8.

High overtones of the OH stretch, such as the fifth at 619 nm and the sixth at 532 nm have been used in studying photoactivated dissociation of *t*-butyl hydroperoxide.<sup>24</sup> Excitation at these wavelengths creates a vibrationally hot electronic ground state.

## 5.6 OH in Carboxylic Acids

### 5.6.1 Overtones

The OH group associated with monomeric carboxylic acid has a sharp non-bonded or free stretching first overtone at about 6920  $\text{cm}^{-1}$  (1445 nm). This band has been observed in the high temperature (92°C) spectrum of octanoic acid.<sup>25</sup> As seen in the inset of Figure 5.9, there is some overlap

of this band with CH combination bands. This overlap appears more pronounced in acids than in alcohols because the acid hydroxyl absorptivity is significantly lower than the alcohol absorptivity. As the temperature is lowered or the solution becomes more concentrated, the formation of dimers with hydrogen-bonded hydroxyl groups broadens the OH stretch overtone and moves it to a lower frequency (longer wavelength) as it does in the mid-IR. This is illustrated in Figure 5.9, a temperature series. Although one can usually observe the broad dimeric hydroxyl band in the mid-IR, in the near IR it appears only to shift the baseline upward in the region from about 1700 nm to at least 2200 nm. Spectral subtraction reveals a very broad and shallow curve in this region.

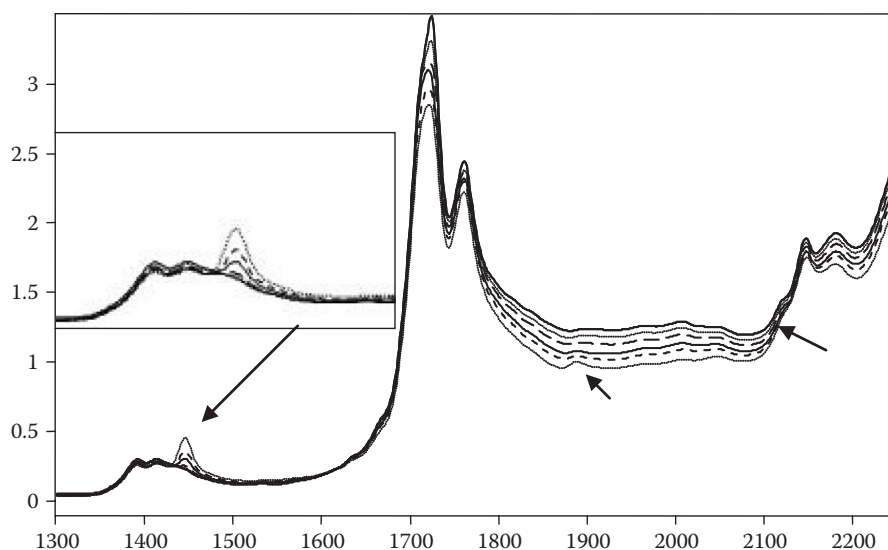
The second overtone of the nonbonded carboxylic acid hydroxyl is at about 10000  $\text{cm}^{-1}$  (1000 nm), and the third at about 12500  $\text{cm}^{-1}$  (800 nm).<sup>26</sup>

### 5.6.2 OH in Carboxylic Acids, Combination Bands

A peak near 5290  $\text{cm}^{-1}$  (1890 nm) due to OH stretch combined with C=O stretch is readily observable in the high temperature curves of Figure 5.9. Also, a doublet at about 4630  $\text{cm}^{-1}$  (2160 nm) and 4695  $\text{cm}^{-1}$  (2130 nm) can be seen. This is due to a CH stretch and C=O stretch combination and has been split because of a rotational mode.

Other, smaller features in the spectrum of monomeric carboxylic acids observed in the gaseous state<sup>27</sup> include small peaks near 8200  $\text{cm}^{-1}$  (1220 nm) due to a combination between the first overtone of the OH stretch and a COH bending mode, 8070  $\text{cm}^{-1}$  (1240 nm) due to the first overtone of the OH stretch and the CO stretch, 7600  $\text{cm}^{-1}$  (1315 nm) due to the first overtone of the OH stretch and OCO bending, and 6500  $\text{cm}^{-1}$  (1540 nm) due to OH stretch and CH stretch.

Additional small peaks include those at about 4950  $\text{cm}^{-1}$  (2020 nm), a combination of the OH stretch and CH bending; 4800  $\text{cm}^{-1}$  (2080 nm), the combination of OH stretch and COH bending; 4710  $\text{cm}^{-1}$  (2120 nm), the combination of CH stretch and C=O stretch; 4680  $\text{cm}^{-1}$  (2140 nm), the combination of OH stretch and CO stretch; 4210  $\text{cm}^{-1}$  (2380 nm), the combination of OH stretch and OCO bending; 4184  $\text{cm}^{-1}$  (2390 nm), the combination of CH stretch and COH bending; and 4050  $\text{cm}^{-1}$  (2470 nm), the combination of CH stretch and CO stretch. All of these assignments



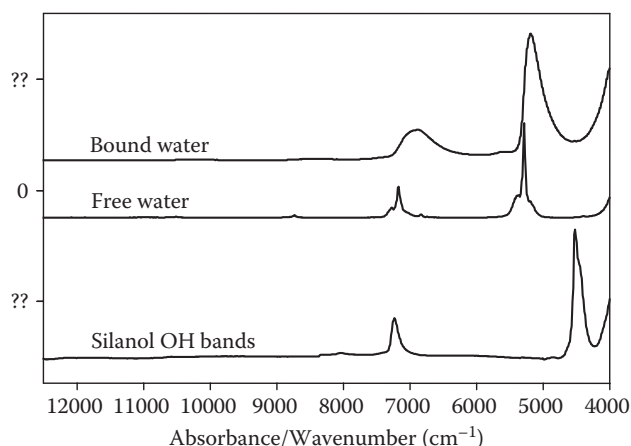
**FIGURE 5.9** Carboxylic acid hydroxyl peaks. Note: Arrows near 1890 and 2130/2160 point out combination bands relating to the nonbonded hydroxyl. (From Weyer, L. G., Lo, S.-C., in *Handbook of Vibrational Spectroscopy*, Chalmers, J. C., Griffiths, P. R., Eds., John Wiley & Sons, New York, 2002. With permission.)

are for formic acid in the gaseous state. Acids with more complex hydrocarbon structures would have more combination bands, and the region from 4000 to 4500  $\text{cm}^{-1}$  (2200 nm to 2500 nm) can become quite complex.

Spectra of dimeric carboxylic acids have a different set of small peaks due to the shifts in the OH and C=O structures. In the gaseous spectrum of formic acid, small peaks appear at about 5630  $\text{cm}^{-1}$  (1780 nm) due to a combination of CH stretch, CH bending, and CO stretch; 4700  $\text{cm}^{-1}$  (2130 nm) due to a combination of C=O stretch and CH stretch; 4500  $\text{cm}^{-1}$  (2220 nm) due to OH stretch and OH---O bending; 4460  $\text{cm}^{-1}$  (2240 nm) due to OH stretch and CH bending; 4340  $\text{cm}^{-1}$  (2300 nm) due to CH stretch and OH---O bending; 4310  $\text{cm}^{-1}$  (2320 nm) due to OH stretch and CO stretch; and 4160  $\text{cm}^{-1}$  (2400 nm) due to CH stretch and COH bending.

## 5.7 Silanols

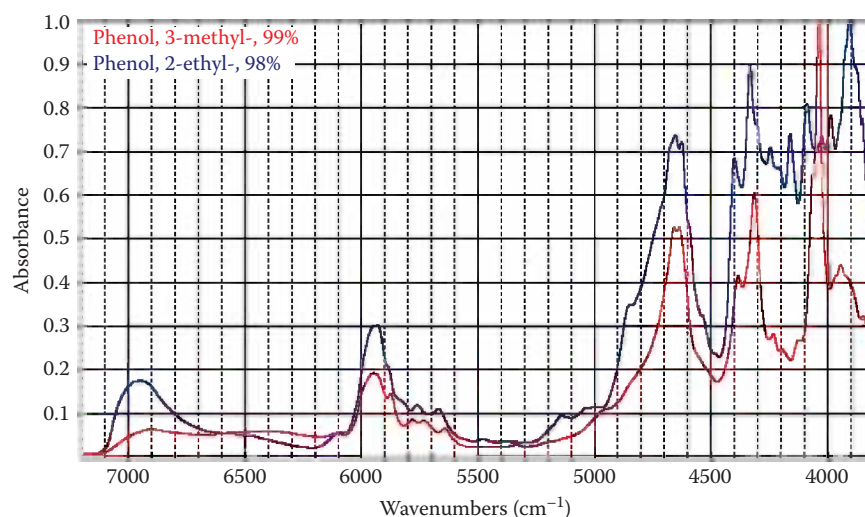
The first overtone of the OH stretch of a silanol group in fused silica optical fibers is at about 7200  $\text{cm}^{-1}$  (1390 nm).<sup>28</sup> This band has been resolved into four peaks, two major and two minor, representing three different OH stretch peaks in different environments and one combination with a 280  $\text{cm}^{-1}$   $\text{SiO}_2$  fundamental that is Raman active. The second overtone shows a similar pattern



**FIGURE 5.10** Comparison of silanol bands in silica with those of water.

centered at about 10600  $\text{cm}^{-1}$  (940 nm) and the third near 13800  $\text{cm}^{-1}$  (725 nm).

Combination band assignments given by Stone and Walrafen for bands at 4100  $\text{cm}^{-1}$  (2440 nm), 4450  $\text{cm}^{-1}$  (2250 nm), and 4520  $\text{cm}^{-1}$  (2210 nm) involve an OH stretch with one of the  $\text{SiO}_2$  fundamentals. Combinations involving twice the frequency of an OH stretch with the SiO stretch near 800  $\text{cm}^{-1}$  were noted at 7920  $\text{cm}^{-1}$  (1260 nm) and 8065  $\text{cm}^{-1}$  (1240 nm), and one band at three times an OH stretch plus the 800  $\text{cm}^{-1}$  band was observed at 11500  $\text{cm}^{-1}$  (850 nm).



**FIGURE 5.11** Two examples of enols as phenols. The top (blue) spectrum is 2-ethyl phenol, and the bottom (red) is 3-methyl phenol. (Spectra used by permission from *NIR Spectra of Organic Compounds*, Wiley-VCH, ISBN 3-527-31630-2.)

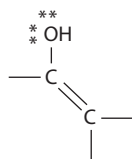
## 5.8 Nitric and Nitrous Acids

The hydroxyl of nitrous (HONO) and nitric (HONO<sub>2</sub>) acids have been studied under various conditions. Aqueous nitric acid solutions that had been extracted into dry carbon tetrachloride showed two prominent hydroxyl peaks at 6826 and 7161 cm<sup>-1</sup> (1465 and 1396 nm).<sup>29</sup> These two peaks are the first overtone of the nitric acid O-H stretch and the water O-H stretch, respectively. These authors also assigned the first and second overtones of the donor O-H stretch of the nitric acid–water complex, among other absorptions. These latter overtones were found at 6062 and 8851 cm<sup>-1</sup> (1650 and 1130 nm), respectively.

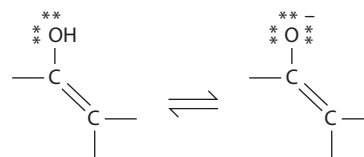
Nitrous acid was examined in gaseous form via cavity ring-down spectroscopy.<sup>30</sup> The O-H stretch + 2 x O-H bend combination band at 6046 cm<sup>-1</sup> (1654 nm) was studied.

## 5.9 Enols and Enolates

The enols contain both unsaturated C=C double bonds as well as an associated O-H group. These alkene-alcohol and associated anions have the general chemical descriptor as:



An enolate is an enol-based anion formed by the presence of an enol in a basic medium. An enolate anion, readily formed in the presence of base is as:



Important NIR bands associated with enols as phenols are the same as those given for phenols.<sup>31</sup> In Figure 5.11 two example enols as phenols are overlaid from 7200 cm<sup>-1</sup> to 3800 cm<sup>-1</sup> (1389 nm to 2632 nm). The measured bands associated with phenols include 3v OH as a broad band from 10200 to 9700 cm<sup>-1</sup>; 2v OH as a broad band from 7200 to 6000 cm<sup>-1</sup>; and the v OH + δ OH combination envelope located at 5000 to 4500 cm<sup>-1</sup>. Specific bands associated with enols are very weak and are mainly associated with C=C-H from the aromatic ring. These can be found in the various chapters and spectra demonstrating aromatic and alkene C-H associated C=C-H bands.

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# Chapter 6

## Water

## 6.1 Water as H<sub>2</sub>O

The analysis of water in various media and under various conditions has been a major part of the field of near-infrared (NIR) spectroscopy since its inception. The strength of the NIR absorption bands, the unique water combination band at 1940 nm, and the sensitivity of the absorption bands to the environment of the water molecules have all contributed to the success of NIR to study and measure water.

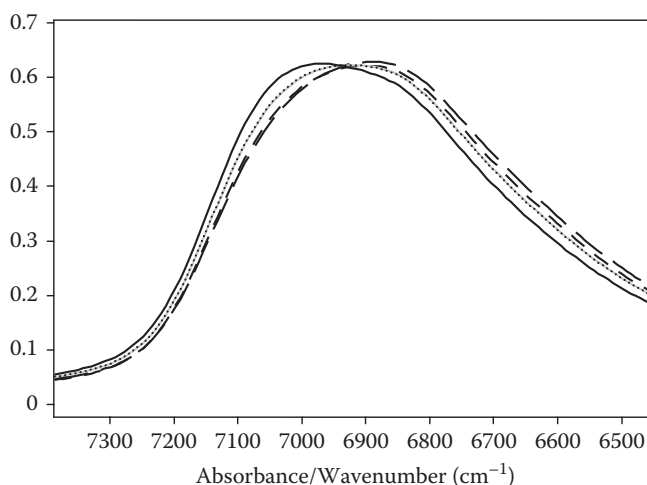
## 6.2 Liquid Water, Ice, and Water Vapor

A summary of the absorption bands of water in the 800–2500 nm region is provided in Table 6.1.<sup>1</sup> The vapor spectral details shown in the table were probably taken from a low-resolution spectrum, as a much larger number of water vapor peaks have been reported by others.<sup>2</sup> As shown in the table, the accepted assignments for the two bands at about 6900 cm<sup>-1</sup> (1450 nm) and 10300 cm<sup>-1</sup> (970 nm) indicate that these are combination bands involving the symmetric and asymmetric stretching modes of the water molecule. This observation has been made by comparison with high-resolution vapor spectra, which show that the combination bands are stronger than the overtones of either the symmetric or asymmetric stretch.<sup>3</sup> This assignment is further supported by consideration of the symmetry group of the vibrations.<sup>4</sup> It has also been suggested that the first overtone of the asymmetric stretch is accidentally degenerate with the sum of asymmetric and symmetric stretches in dilute solutions.<sup>5</sup> Therefore,

although these two bands are generally referred to as the first and second overtones of the OH stretch, they are actually combination bands.

The strong  $5150\text{ cm}^{-1}$  (1940 nm) peak is a combination of the asymmetric stretch and bending of the water molecule. In liquid water, there are also weak, broad combination bands near  $5620\text{ cm}^{-1}$  (1780 nm) and  $8310\text{ cm}^{-1}$  (1200 nm) and a second set near 11800 and  $13000\text{ cm}^{-1}$  (840 and 740 nm).

The water peaks with maxima near 10300  $\text{cm}^{-1}$  (970 nm),<sup>7</sup> 8330  $\text{cm}^{-1}$  (1200 nm),<sup>3,7</sup> and 6900  $\text{cm}^{-1}$  (1450 nm) at room temperature shift toward higher wavenumber (lower wavelength) with increasing temperature, and appear to consist of an unresolved pair of peaks with an isosbestic point between them. See Figure 6.1 for an

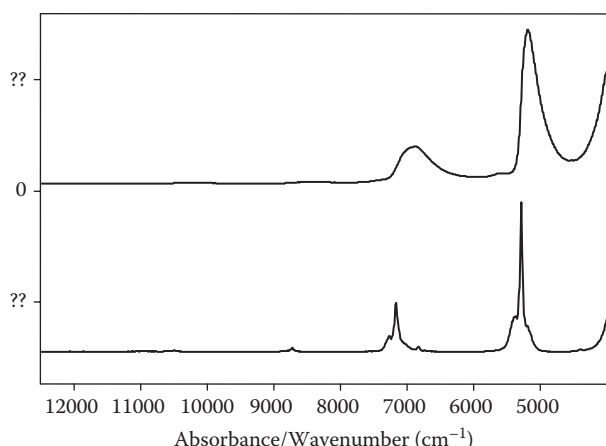


**FIGURE 6.1** Water spectra at five temperatures from 25°C to 65°C.

### Table 6.1 Absorption Peaks of Water, Ice, and Vapor

| Ice (nm) | Ice (cm <sup>-1</sup> ) | Liquid Near Freezing Point (nm) | Liquid Near Freezing Point (cm <sup>-1</sup> ) | Liquid Near Boiling Point (nm) | Liquid Near Boiling Point (cm <sup>-1</sup> ) | Vapor (nm) | Vapor (cm <sup>-1</sup> ) | Assignment          |
|----------|-------------------------|---------------------------------|--|--------------------------------|---|------------|---------------------------|---------------------|
| 800      | 12500                   | 770                             | 13000  | 740                            | 13500   | 723        | 13831                     | 3 $v_1 + v_3$       |
| 909      | 11000                   | 847                             | 11800  | 840                            | 11900   | 823        | 12151                     | 2 $v_1 + v_2 + v_3$ |
| 1025     | 9760                    | 979                             | 10210  | 967                            | 10340   | 942        | 10613                     | 2 $v_1 + v_3$       |
| 1250     | 7990                    | 1200                            | 8310   | 1160                           | 8640  | 1135       | 8807                      | $v_1 + v_2 + v_3$   |
| 1492     | 6700                    | 1453                            | 6880   | 1425                           | 7020  | 1380       | 7252                      | $v_1 + v_3$         |
| 1780     | 5620                    | 1780                            | 5620   | 1786                           | 5600  | —          | —                         | $v_2 + v_3 + v_L$   |
| 1988     | 5030                    | 1938                            | 5160   | 1916                           | 5220  | 1875       | 5332                      | $v_2 + v_3$         |

*Note:* For this table, n1 is the symmetric stretch of the water molecule, n2 is the bending mode, and n3 is the asymmetric stretch. nL was not defined in the original reference. It has been postulated to be an “intermolecular mode” (see reference 6).

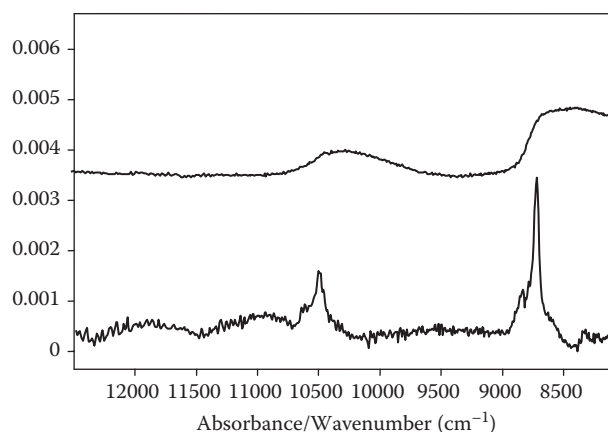


**FIGURE 6.2** Free and bonded water spectra liquid water is shown in the top spectrum and water in carbon tetrachloride in the bottom spectrum.

illustration of the temperature effect at the “first overtone.” The isosbestic point for the 10300  $\text{cm}^{-1}$  (970 nm) band is 10100  $\text{cm}^{-1}$  (990 nm), for the 8330  $\text{cm}^{-1}$  (1200 nm) is about 8400  $\text{cm}^{-1}$  (1190 nm),<sup>3</sup> and for the 6900  $\text{cm}^{-1}$  (1450 nm) band is at about 6960  $\text{cm}^{-1}$  (1440 nm).<sup>4</sup> The presence of an isosbestic point indicates that NIR calibrations for water independent of temperature may be possible by judicious wavelength choice.

An isosbestic point has also been studied for pressure changes of water at constant temperature.<sup>7</sup> A shift to higher wavenumber (lower wavelength) occurred with increasing pressure. The pressure isosbestic point for the 10300  $\text{cm}^{-1}$  peak was at about 10200  $\text{cm}^{-1}$  (980 nm).

There has been some controversy over whether liquid water contains water molecules in three states of hydrogen bonding: free, bonded through one, two, or three hydrogen bonds; or is a continuum of different bond strengths or



**FIGURE 6.3** Water spectra, higher frequency region. Liquid water is shown in the top spectrum and water in carbon tetrachloride in the bottom spectrum.

somewhere in between.<sup>8</sup> In general, temperature studies and data treatments such as second derivatives and spectral resolution have indicated that there are separate peaks present for different states of hydrogen-bonded water molecules.<sup>9</sup> As pointed out by Maeda et al.,<sup>9</sup> the intensities and width of these peaks are affected by the anharmonicity of each, so that the molecules bonded to more adjacent molecules, having less anharmonicity, will be broader and weaker.

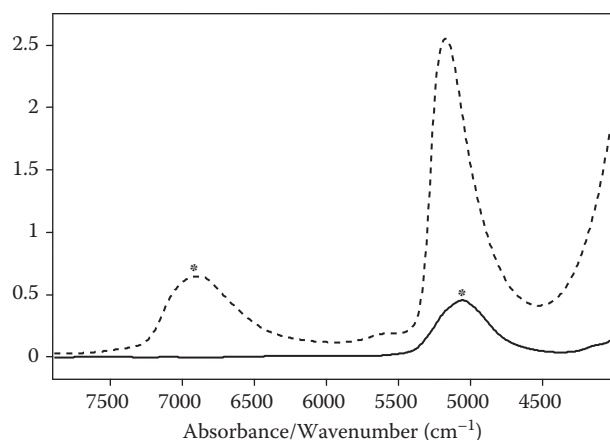
Figure 6.2 and Figure 6.3 show the spectra of liquid water and water in a “free” state, in carbon tetrachloride.

### 6.3 Deuterium Oxide ( $\text{D}_2\text{O}$ )

The NIR spectrum of fully deuterated water is very similar to that of  $\text{H}_2\text{O}$ , except that the peaks are all shifted because of the mass difference of the hydrogen atom. Table 6.2

**Table 6.2** Band Assignments for  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , and  $\text{HDO}$

| Liquid $\text{H}_2\text{O}$ Near Freezing Point (nm) | Liquid $\text{H}_2\text{O}$ Near Freezing Point ( $\text{cm}^{-1}$ ) | Liquid $\text{D}_2\text{O}$ (nm) | Liquid $\text{D}_2\text{O}$ ( $\text{cm}^{-1}$ ) | Liquid $\text{HDO}$ (nm) | Liquid $\text{HDO}$ ( $\text{cm}^{-1}$ ) | Assignment                |
|--|--|----------------------------------|--|--------------------------|--|---------------------------|
| 770  | 13000  | —                                | —  | —                        | —  | $3 \nu_1 + \nu_3$         |
| 847  | 11800  | 1190                             | 8400   | 1000                     | 10000                                    | $2 \nu_1 + \nu_2 + \nu_3$ |
| 979  | 10210  | 1340                             | 7470   | 1240                     | 8065                                     | $2 \nu_1 + \nu_3$         |
| 1200   | 8310   | 1620                             | 6165   | —                        | —  | $\nu_1 + \nu_2 + \nu_3$   |
| 1453   | 6880   | 1970                             | 5080   | 1670                     | 5975                                     | $\nu_1 + \nu_3$           |
| 1780   | 5620   | 2440                             | 4100   | —                        | —  | $\nu_2 + \nu_3 + \nu_L$   |
| 1938   | 5160   | 2600                             | 3830   | 2020                     | 4945                                     | $\nu_2 + \nu_3$           |



**FIGURE 6.4** Comparison of water and deuterium oxide. Dotted curve is water and solid curve is deuterium oxide. Asterisks indicate the  $\nu_1 + \nu_3$  combination band in both.

summarizes the absorptions.<sup>10</sup> Figure 6.4 shows a portion of the NIR spectral region, illustrating the isotope shift of the  $\nu_1 + \nu_3$  combination band (indicated by asterisks).

HDO is not of the same symmetry group as  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , and therefore its peak shifts are not strictly isotope shifts. Also, liquid HDO is in equilibrium with  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , and the contributions from these molecules must be subtracted in order to observe the spectrum of HDO. Note that the large combination band used most often for moisture measurement is out of the normal NIR range for deuterium oxide.

## 6.4 Water in Various Solvents

The structure of water and the band assignments of water in various solvents has been studied extensively in the NIR. The  $5155\text{ cm}^{-1}$  ( $1940\text{ nm}$ ) combination band in particular has been very useful for studies and analyses of water in the presence of hydroxyl-containing solvents because it is usually well isolated.

The position and widths of the bands vary predictably with the degree of hydrogen bonding and the basicity of the solvent.<sup>11</sup> Interactions are strongest in dimethyl sulfoxide (DMSO) and weakest in nitromethane, as demonstrated by the position of the  $5155\text{ cm}^{-1}$  ( $1940\text{ nm}$ ) peak. The series of solvents includes, in order: DMSO, dioxane, acetone, acetonitrile, and nitromethane, and the peak maximum ranged from  $5150\text{ cm}^{-1}$  ( $1942\text{ nm}$ ) to  $5270\text{ cm}^{-1}$  ( $1898\text{ nm}$ ).<sup>12</sup> The effect of low levels of ethanol added to water was seen to be qualitatively the same as a temperature effect.<sup>13</sup>

In all solvents, the fraction of free water was greater in both dilute solution and in neat water than it was in intermediate concentrations. Through the analysis of ternary mixtures, the amount of nonbonded water molecules was found to be negligibly small in proton-acceptor solvents.

## 6.5 Water in Other Matrices, Including Glasses

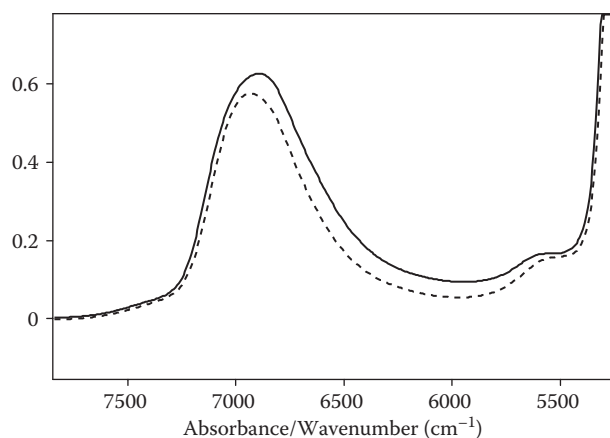
The relative position of the water bands has provided a good deal of information to researchers. In studying protein denaturation, for example, the symmetric stretch–asymmetric stretch combination band provided information on the state of the water during the reaction. The shift from  $1410\text{ nm}$  to  $1490\text{ nm}$  indicated an increase in bound water.<sup>14</sup> In studying water sorption on PET film, the same spectral region showed that water was not interacting with the film. The wavelengths of the subbands in that region were all lower than those in bulk water.<sup>15</sup> The total water content of starch and cellulose was compared to the “water activity” using the  $1450$  and  $1940\text{ nm}$  bands.<sup>16</sup> It was found that NIR could discriminate between different levels of moisture content at the same activity but not very well between activities at the same moisture content. The  $1940\text{ nm}$  band was also used in a cell adhesion study.<sup>17</sup>

Water absorption patterns in biological systems have generated a great deal of interest and attempts to collect and catalog the information in order to better understand natural phenomena. R. Tsenkova coined the term “aquaphotomics” to describe these water-interaction studies.<sup>18</sup>

Water incorporated into fused silica is of considerable importance because the resulting silanol groups affect the NIR transmission of silica optical fibers and other optical components. Silanols are discussed in the OH chapter (Section 5.7). In mixed glasses, such as those containing borosilicates and aluminosilicates, associated water OH groups give rise to diffuse absorption bands.<sup>19</sup> The absorption bands of water molecules on silica surfaces have been described by Klier et al.<sup>20</sup>

## 6.6 Ionic Species in Water

There are several ways that ionic species in water affect NIR spectra. These effects include (1) a decrease in the concentration of water; (2) charge-dipole interactions

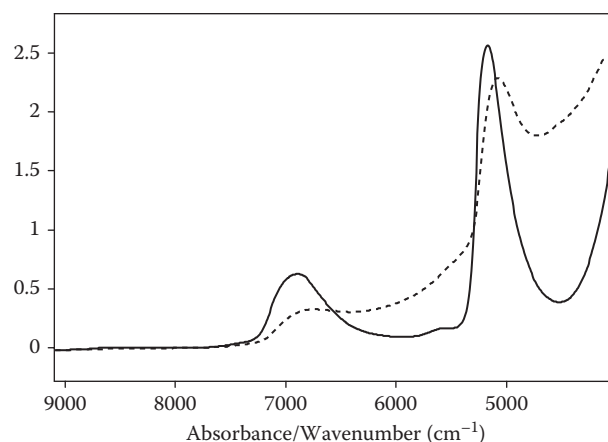


**FIGURE 6.5** The effect of dissolved sodium chloride on the water spectrum. The solid curve is pure water and the dotted curve is 20% NaCl.

between the ions and the water molecules, which affect the hydrogen-bonding of the water itself; (3) the formation of hydrogen bonds between an oxygen or nitrogen in the ions and water; (4) the presence of OH itself or OH within an ion (such as  $\text{HCO}_3^-$ ); and (5) the presence of another specific NIR-active functional group within the ion (such as acetate's CH and ammonia's NH), and the condition by which some ions produce OH or H through hydrolysis (such as  $\text{CO}_3^{=}$ ).<sup>21</sup> In addition, the color of some ions can extend into the NIR region.

One example of an ionic interaction with water molecules is shown in Figure 6.4. Sodium chloride alone in water can be readily measured in spite of its having no NIR bands of its own, because it affects the spectrum of water by reducing the amount of hydrogen bonding within the bulk water.<sup>22,23</sup> The salt lowers the intensity of the water peak and also shifts it to the left, toward higher frequencies indicating less hydrogen bonding.

Different ions have somewhat different effects, depending on their size and electronic characteristics. Thermodynamic calculations have indicated that divalent magnesium ions, trivalent aluminum ions, and protons enhance the structural order of the water, whereas monovalent sodium and potassium disrupt it.<sup>24</sup> Differences in the intensities of changes to the NIR spectra have been attributed to the charge-to-radius ratios of cations or anions.<sup>21</sup> An example of the effect of a proton is shown in the HCl spectrum in Figure 6.6. Note the shift toward the lower

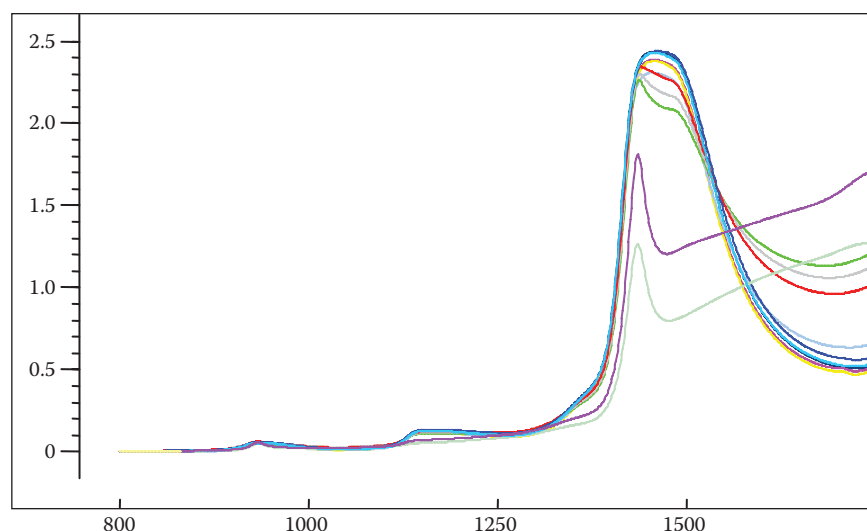


**FIGURE 6.6** Spectrum of concentrated HCl (dotted curve) compared to pure water in a 0.5 mm pathlength cell.

wavenumber, indicating an increase in hydrogen bonding. Hydroxide and fluoride anions are said to enhance the structure, whereas chloride, bromide, nitrite, and isocyanate disrupt it.<sup>25</sup> Choppin and Buijs based their assessment of structure effects on the  $8330\text{ cm}^{-1}$  ( $1200\text{ nm}$ ) combination band by calculating the relative intensities of the free, singly bonded and doubly bonded peaks. Measurements of pH and titration endpoints by NIR based on the effects on the water peaks have been reported.<sup>24</sup>

The ionic hydroxyl group in aqueous solutions has its own specific absorption bands with first and second overtone bands at  $7040\text{ cm}^{-1}$  ( $1421\text{ nm}$ ) and  $1034\text{ cm}^{-1}$  ( $967\text{ nm}$ ).<sup>26,27</sup> Also, a broad band centered at about  $1100\text{ nm}$  has been attributed to the binding of two water molecules to the hydroxide ion. As the hydroxide concentration is increased above 5 molal, the water peaks at  $6900\text{ cm}^{-1}$  ( $1450\text{ nm}$ ) and  $1025\text{ cm}^{-1}$  ( $976\text{ nm}$ ) decrease, and the hydroxide ion peaks at  $1421$  and  $967\text{ nm}$  become prominent. This effect is complicated, however, and involves water activity and the ability of the solutes to confine the bulk solvent within hydration spheres. KOH solutions do not behave the same as NaOH solutions, and the effects of the cation on the water absorption need to be accounted for to obtain good measurements of hydroxide. Figure 6.7 illustrates the prominent ionic hydroxyl peak near  $7040\text{ cm}^{-1}$  ( $1421\text{ nm}$ ). It is especially noticeable in the 50% solution.





**FIGURE 6.7** Sodium hydroxide solutions, 0%–50% NaOH. The bottom curve is 50% NaOH and the top is pure water.

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# Chapter 7

## Carbonyls

## 7.1 Organic Carbonyl Compounds: Overtones

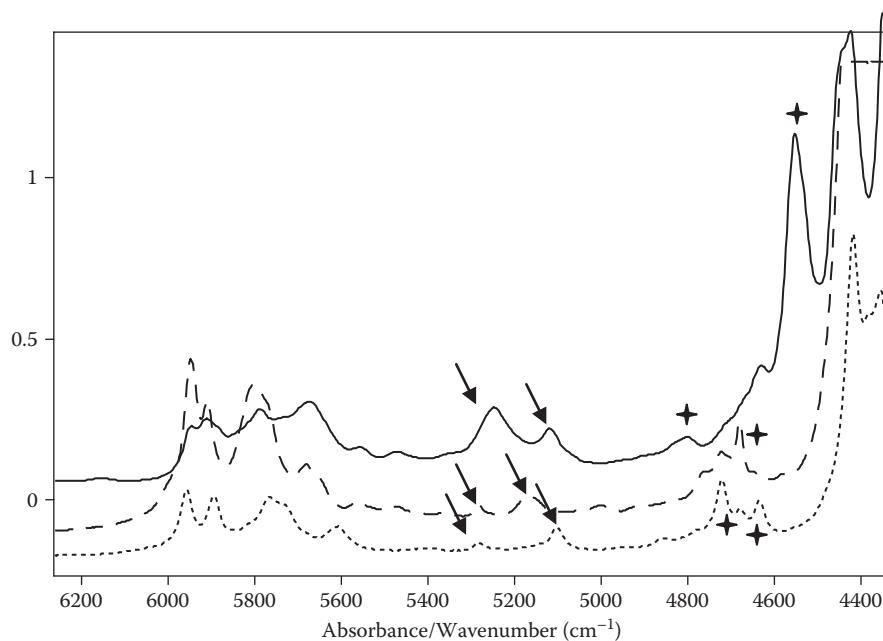
Aldehydes, ketones, esters, anhydrides, acid chlorides and carboxylic acids show some near-infrared (NIR) carbonyl associated bands, as illustrated in Figure 7.1. The C=O stretch is very strong in the mid-IR; so even though the first overtone is still in the mid-IR region, the second overtone may be strong enough to observe in the NIR. Although the second overtones are relatively weak and would be overwhelmed if any water was present, there are some anhydrous situations in which it might be useful to analyze carbonyl compounds by NIR spectroscopy.

As in the mid-IR, the position of the C=O varies with the environment of the group. The position or frequency of the fundamental carbonyl C=O stretching vibration is affected by (1) the isotope effects and mass change of substituted groups, (2) bond angles of substituted groups, (3) electronic (resonance and inductive) effects, and (4) interactions of these effects. Substituents with higher mass decrease the C=O stretch frequency; increasing the mass or bond angles of substituents also decreases the fundamental band frequency by up to 40  $\text{cm}^{-1}$  at 1715  $\text{cm}^{-1}$ . Similarly, decreasing the substituent mass, or bond angles

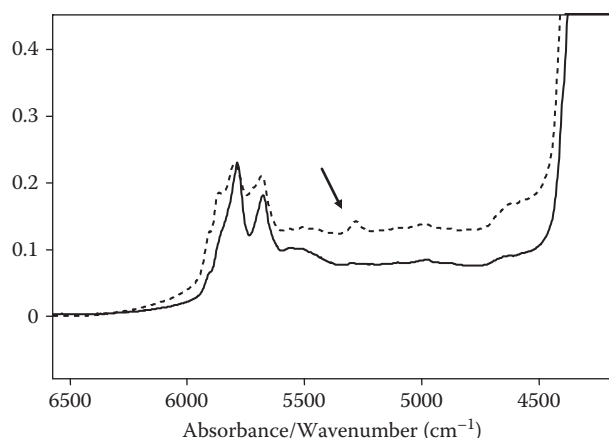
between the carbonyl carbon and its substituents increases the frequency by 25  $\text{cm}^{-1}$  above the nominal 1715  $\text{cm}^{-1}$  carbonyl C=O stretch frequency. More electronegative (electron withdrawing) substituents will increase the carbonyl carbon-oxygen stretch frequency by up to 100  $\text{cm}^{-1}$  above the 1715  $\text{cm}^{-1}$  nominal frequency. Conjugation of the carbonyl group to aromatic or olefinic groups tends to lower the frequency for both C=O and C=C by 30 to 40  $\text{cm}^{-1}$  dependent upon the ring size of the substituent.

In general, the position of the second overtone of the carbonyl of simple noncyclic aliphatic compounds shifts to lower wavelength in the series: acid chlorides, anhydrides, carboxylic acid monomer, lactones, aldehydes, ketones, and esters. Amide carbonyl second overtones are overwhelmed by bands that involve NH stretch, and cannot therefore be included in this comparison. An acid chloride second overtone is at 5400  $\text{cm}^{-1}$  (1850 nm), propionaldehyde is at 5100  $\text{cm}^{-1}$  (1960 nm), acetone is at 5100  $\text{cm}^{-1}$  (1960 nm); with an additional split band at 5260  $\text{cm}^{-1}$  (1900 nm), and ethyl acetate is at 5160  $\text{cm}^{-1}$  (1940 nm).

In polyethylene terephthalate (PET), the ester carbonyl second overtone occurs at 5115–5125  $\text{cm}^{-1}$  (1955–1951 nm), depending on the crystallinity of the sample.<sup>1</sup>



**FIGURE 7.1** Comparison of different types of carbonyl compounds. Note: The solid curve is neat propionaldehyde, dashed curve is ethyl acetate in  $\text{CCl}_4$ , dotted curve is neat acetone. Arrows indicate the carbonyl second overtone doublets and stars indicate combination bands involving the carbonyls.



**FIGURE 7.2** Illustration of acid carbonyl second overtone; octanoic acid (dotted curve) and octadecanoic acid (solid).

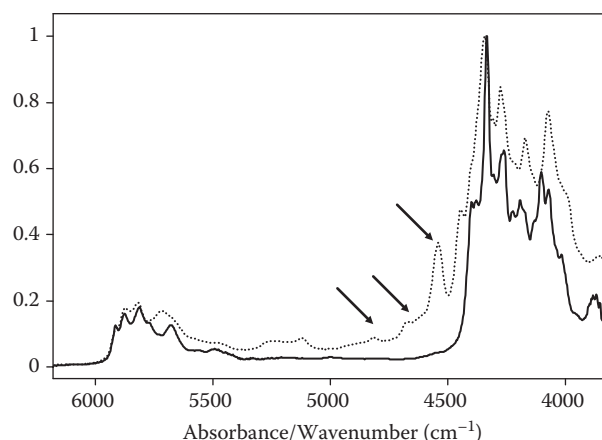
Conjugation with aromatic rings and double bonds, and interactions with halogens and cyclic structures all affect the band positions, as in the mid-IR. Also, these second overtones are sometimes split into two, as there may be two or more small bands in the vicinity of the calculated second overtone.<sup>2</sup> The second overtone of the C=O of a carboxylic acid appears at about 5260  $\text{cm}^{-1}$  (1900 nm) and is particularly clear in a spectrum of perfluorocaproic acid taken in solution, as this acid has no CH absorptions.<sup>3</sup> It can be seen in Figure 7.2, a comparison between octanoic and octadecanoic acids in carbon tetrachloride. With the shorter-chain acid, the acid carbonyl peak is more prominent.

The CH stretch overtones of aldehydes should be observed at shorter wavenumbers than most compounds as they are in the mid-IR. They are not very distinctive however. In the mid-IR region, the CH stretch is usually a doublet and involves interaction with an overtone of a bending mode.<sup>4</sup> Therefore, it is not likely to be very strong in the near IR.

The CH stretch of benzaldehyde's alkyl is at 5376  $\text{cm}^{-1}$  (1860 nm).<sup>5</sup> It is very weak, possibly due to perturbation by a combination band.

## 7.2 Organic Carbonyl Compounds: Combination Bands

In addition to the overtones, there are some combination bands that include the C=O stretch. Combination bands involving C=O and CH in ketones are weak, if they exist



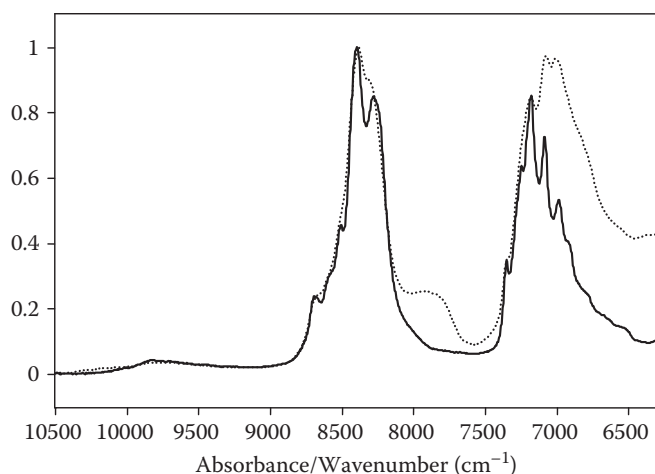
**FIGURE 7.3** Pentane (solid curve) and pentanal (dotted curve) compared. Combination bands are indicated with arrows and are described in the text.

at all, because the two groups do not share a common carbon atom. In aldehydes and formates, however, there is a carbon atom with both a proton and an oxygen atom attached, which gives rise to a combination band in the region of 4760–4445  $\text{cm}^{-1}$  (2100–2200 nm).<sup>3,6</sup> The strong formate ester band at 4650  $\text{cm}^{-1}$  (2150 nm) was assigned to CH stretch and C=O stretch by a deuteration study.<sup>7</sup>

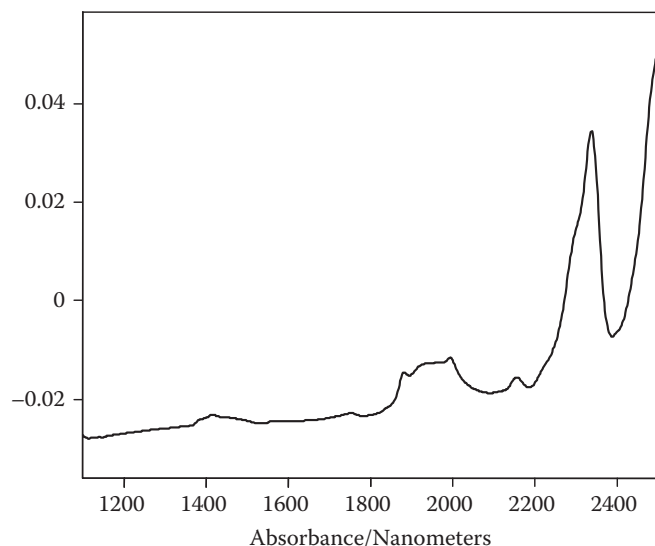
In one study of short-chain aliphatic aldehydes, the CH stretch–C=O stretch combination band was given as a peak at 4504  $\text{cm}^{-1}$  (2220 nm) and a 2x CH bend (in-plane rocking) plus the carbonyl stretch at about 4514  $\text{cm}^{-1}$  (2215 nm).<sup>8</sup> These appear to be one peak in Figure 7.3. Also a peak near 4888  $\text{cm}^{-1}$  (2045 nm) was assigned as 2xC=O stretch plus 2x CH bending (out-of-plane wagging)<sup>9</sup> and one at 4748  $\text{cm}^{-1}$  (2106 nm) was assigned as a combination of CH bending (in-plane rocking) and C=O stretching. Figure 7.3 illustrates these absorption peaks. There is also an aldehyde-associated peak near 7850  $\text{cm}^{-1}$ , as seen in Figure 7.4 and aldehyde spectra found in the appendices. This could be a second overtone involving the 2700  $\text{cm}^{-1}$  fundamental CH peak. However, the fundamental CH stretch absorption is split by Fermi resonance and therefore near IR peaks are probably also complicated by Fermi resonance.

## 7.3 Carbonate

The inorganic ion  $\text{CO}_3^{2-}$  has been analyzed in the NIR region in many geological studies. It has two strong bands of particular usefulness near 3920 and 4255  $\text{cm}^{-1}$



**FIGURE 7.4** Pentane (solid curve) and pentanal (dotted curve) in the short wavelength region.



**FIGURE 7.5** Reflection spectrum of powdered calcium carbonate.

(2550 and 2350 nm, respectively). The  $3920\text{ cm}^{-1}$  band is most likely due to the sum of an infrared-forbidden symmetric stretch and twice the asymmetric stretch ( $n_1 + 2n_3$ ). The  $4255\text{ cm}^{-1}$  has been assigned as the second overtone of the strong asymmetric stretch ( $3n_3$ ).<sup>10,11</sup> Figure 7.5 clearly shows the strong  $4255\text{ cm}^{-1}$  (2350 nm) band.

The band positions shift with environment and are in different positions in calcium carbonate (polymorphs calcite and aragonite), dolomite (calcium magnesium

**Table 7.1 Carbonyl 1—Isocyanate Band Assignments**

| Wavenumber ( $\text{cm}^{-1}$ ) | Wavelength ( $\mu\text{m}$ ) | Assignment  |
|---------------------------------|------------------------------|---|
| 4872                            | 2052                         | $2 \times \delta (\text{NCO}) + \nu (\text{NCO})$ |
| 5220                            | 1915                         | $\nu (\text{NCO}) + \nu \text{CH}$                |

carbonate), sodium carbonate, and so forth, alone or in aqueous solutions.

## 7.4 Isocyanates

Table 7.1 provides some band assignments made for the isocyanate group  $\text{N}=\text{C}=\text{O}$ .<sup>12</sup>

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# Chapter 8

## **Amines and Amides**

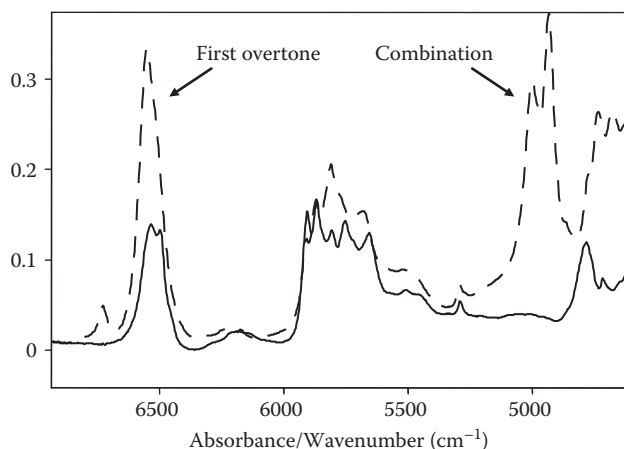
## 8.1 N-H Functional Groups

The N-H functional group found in amines and amides has not been studied as extensively as hydroxyls, but it is important because it appears in many natural products, pharmaceuticals, and polymers. N-H participates in hydrogen bonding, and therefore behaves differently in various solvents and matrices. The near-infrared (NIR) region offers a special advantage in the measurement of the primary amine group  $\text{NH}_2$  due to a unique combination band.

## 8.2 Aliphatic Amines: Overtone Regions

As shown in Figure 8.1, primary, secondary, and tertiary amines are distinctly different in the first overtone region near  $6600\text{ cm}^{-1}$ . Primary amines have a doublet, secondary a single peak, and tertiary has no peak as it has no N-H functionality. The asymmetric and symmetric NH stretching peaks occur at  $6730$  and  $6553\text{ cm}^{-1}$  ( $1486$  and  $1625\text{ nm}$ ), respectively, in butyl amine in carbon tetrachloride. The first overtone of secondary amines has only one band near  $6530\text{ cm}^{-1}$  ( $1530\text{ nm}$ ).

Figure 8.1 shows a primary and a secondary amine in dilute carbon tetrachloride solution. The NH stretch first overtones broaden and shift to longer wavelengths with an increase in concentration and shift slightly in other solvents. It has been reported that the band position does not



**FIGURE 8.1** Primary and secondary aliphatic amines, n-butyl amine (dashed line) and di-isobutyl amine (solid line).

change with temperature in the range of  $70$ – $120^\circ\text{C}$  in contrast with the hydroxyl group.<sup>1</sup> The symmetric absorption of the  $-\text{NH}_2$  group is much more intense ( $\sim 6$  to  $7$  times) than the asymmetric absorption.<sup>2</sup>

Polar groups next to the amine tend to displace the first overtone. An amine next to phosphorus has its first overtone at  $6720$  ( $1488\text{ nm}$ ) and  $7652\text{ cm}^{-1}$  ( $1481\text{ nm}$ ).<sup>1</sup>

In the mid-IR region, the amine NH stretch absorption is weak relative to primary alcohols, about  $1$ – $2\text{ L/mole}\cdot\text{cm}$  compared to  $50$ – $100\text{ L/mole}\cdot\text{cm}$ .<sup>3</sup> However, the intensity of the first overtone of aliphatic amines is of the same order of magnitude as the fundamental. For example, n-butyl amine's first overtone has an absorptivity of  $0.6\text{ L/mole}\cdot\text{cm}$  compared to  $2.4\text{ L/mole}\cdot\text{cm}$  for the fundamental. The overtones of amines and hydroxyls are of about the same magnitude, and it may be easier to detect an amine in the presence of alcohols in the NIR than the mid-IR.

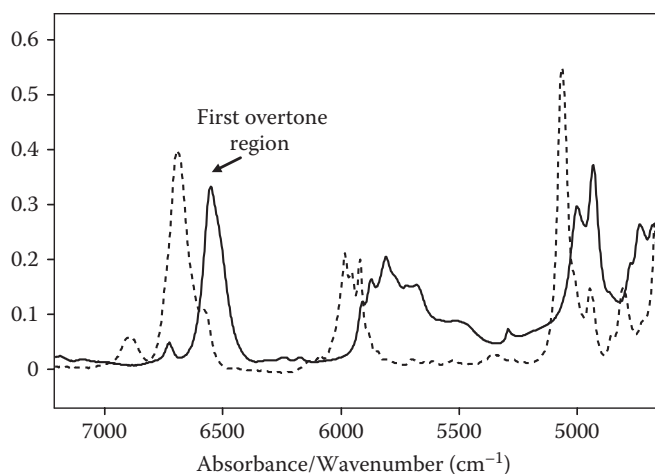
A single peak that occurs near  $9700\text{ cm}^{-1}$  ( $1035\text{ nm}$ ) has been assigned to the second overtone of  $-\text{NH}_2$ . The third overtone occurs as a doublet at  $12407$  and  $12837\text{ cm}^{-1}$  ( $806$  and  $779\text{ nm}$ ). The absorption of the latter band is also stronger and its intensity increases with increasing chain length. The fourth overtone appears as a doublet near  $15129\text{ cm}^{-1}$  ( $661\text{ nm}$ ), but one of the pair is of much lower intensity.<sup>1</sup>

### 8.2.1 Combinations

The first combination band region of primary amines, which derives from the N-H stretching modes and the deformation or scissoring of the  $\text{NH}_2$  group, has been found to be very useful in quantitative and qualitative analyses. As shown in Figure 8.1, n-butyl amine has a strong doublet in  $\text{CCl}_4$  near  $5000\text{ cm}^{-1}$  that is totally absent in secondary (or tertiary) amines. This feature is not a doublet in all solvents, and its dual nature has been attributed to interaction with the solvents. It is a single peak in benzene and hexane, but a double peak in mixtures of benzene and chloroform.<sup>4</sup> The lower frequency peak increases upon addition of more polar solvents, and its position has been used to study solvent associations.<sup>5</sup> Sinsheimer and Keuhnelian have interpreted the doublet as being due to a free (higher wavenumber) and a hydrogen-bonded band (lower wavenumber).<sup>6</sup>

A second set of combination bands has been reported at  $12000$  and  $12380\text{ cm}^{-1}$  ( $832$  and  $808\text{ nm}$ ) in secondary amines.<sup>1</sup>





**FIGURE 8.2** Aniline (dotted line) compared to *n*-butylamine (solid line).

### 8.3 Aromatic Amines: Overtones

The NH stretching bands of aromatic amines, such as aniline, show a doublet in the first overtone region, but it is shifted to lower wavelengths relative to aliphatic amines. Figure 8.2 compares the NIR spectrum of aniline in CCl<sub>4</sub> with that of *n*-butylamine. The asymmetric vibration occurs at 6890 cm<sup>-1</sup> (1450 nm) and the symmetric band is in the region of 6685 cm<sup>-1</sup> (1496 nm). In studies of ring-substituted derivatives, Whetsel et al. have investigated the correlation of substituent electronic nature with band positions and intensities in both NH stretching and combination modes.<sup>7</sup> The shifts of NH overtone bands may be observed as effects of various solvents and temperature conditions.

As in the case of the aliphatic amines, secondary aromatic amines show only one NH stretching overtone. For *N*-butyl aniline in CCl<sub>4</sub>, for example, the overtone is at 6675 cm<sup>-1</sup> (1498 nm). The effects of hydrogen bonding on the mechanical anharmonicity of the NH stretching vibration of *N*-methylaniline have been reported.<sup>8</sup>

In heterocyclic aromatic amines, such as pyrroles, indoles, and carbazoles, there is a first overtone NH stretching between 6803 cm<sup>-1</sup> (1470 nm) and 6897 cm<sup>-1</sup> (1440 nm).<sup>9</sup> Unlike the aliphatic amines, where the intensity of the overtone is approximately the same as the intensity of the fundamental, the aromatic and heterocyclic amines have a much greater absorptivity difference between fundamental and overtone. The overtone intensities do not vary widely, but the intensities of the fundamentals vary by a factor of about 100 from aliphatic to heterocyclic. Table 8.1 lists some of the intensities, given in peak area.

Table 8.2 lists band positions and intensities of some primary aromatic amines in carbon tetrachloride, illustrating the effect of substituents.<sup>10</sup> The table also includes the second overtone band positions. Molar absorptivities, generally around 1.3 L/mole-cm for the symmetric band, around 0.15 for the asymmetric, and 0.03 for the second overtone, were also provided in the reference.

The self-association of aromatic amines in various solvents and temperatures has been studied extensively and has been summarized by Whetsel.<sup>11</sup> The formation of dimers and higher-order associations has been proposed. Association in carbon tetrachloride occurs and some authors have found chloroform to be a better choice for analyzing amines in general.

**Table 8.1 Secondary Amine First Overtone Band Intensity Comparisons, CCl<sub>4</sub> Solution, Area in Units of cm<sup>2</sup> mole<sup>-1</sup> second<sup>-1</sup>**

| Compound              | Area of Fundamental × 10 <sup>9</sup> | Area of First Overtone × 10 <sup>9</sup> | Ratio of Areas | Position of Overtone (cm <sup>-1</sup> ) |
|-----------------------|---------------------------------------|--|----------------|--|
| Dimethylamine (vapor) | ~6                                    | 9.5                                      | ~0.6           | 6580                                     |
| Diethylamine          | ~3.5                                  | ~4.8                                     | ~0.7           | 6471                                     |
| Morpholine            | 21                                    | 10                                       | 2.1            | 6536                                     |
| Dibenzylamine         | 30                                    | 6.2                                      | 4.9            | 6490, 6512, 6534                         |
| <i>N</i> -benzylamine | 183                                   | 7.5                                      | 24             | 6751                                     |
| Diphenylamine         | 228                                   | 5.6                                      | 40             | 6729                                     |
| Indole                | 568                                   | 11.2                                     | 59             | 6844                                     |
| Carbazole             | 550                                   | 8.8                                      | 62             | 6826                                     |

**Table 8.2 Example Aromatic Amine Band Overtones**

| Substituent        | First Overtone Symmetric (cm <sup>-1</sup> ) | First Overtone Symmetric (nm) | First Overtone Asymmetric (cm <sup>-1</sup> ) | First Overtone Asymmetric (nm) | Second Overtone (cm <sup>-1</sup> ) | Second Overtone (nm) |
|--------------------|--|-------------------------------|---|--------------------------------|-------------------------------------|----------------------|
| p-NH <sub>2</sub>  | 6656   | 1502.5                        | 6852  | 1459.5                         | 9741                                | 1026.5               |
| p-CH <sub>3</sub>  | 6683   | 1496.5                        | 6885  | 1452.5                         | 9775                                | 1023.0               |
| None               | 6698   | 1493.0                        | 6904  | 1448.5                         | 9794                                | 1021.0               |
| p-Cl               | 6705   | 1491.5                        | 6906  | 1448.0                         | 9813                                | 1019.0               |
| m-Cl               | 6713   | 1489.5                        | 6920  | 1445.0                         | 9818                                | 1018.5               |
| m-NO <sub>2</sub>  | 6725   | 1487.0                        | 6940  | 1441.0                         | 9852                                | 1015.0               |
| o-OCH <sub>3</sub> | 6700   | 1492.5                        | 6916  | 1446.0                         | 9818                                | 1018.5               |
| o-Cl               | 6705   | 1491.5                        | 6930  | 1443.0                         | 9828                                | 1017.5               |
| o-NO <sub>2</sub>  | 6791   | 1472.0                        | 6982  | 1432.0                         | 9970                                | 1003.0               |

**Table 8.3 Example Combination Band Positions**

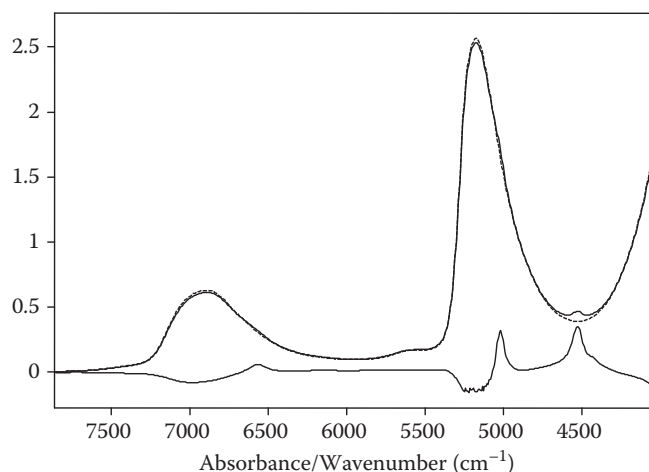
| Substituent        | Combination Band (cm <sup>-1</sup> ) | Combination Band (nm) |
|--------------------|--------------------------------------|-----------------------|
| p-NH <sub>2</sub>  | 5049                                 | 1980.5                |
| p-CH <sub>3</sub>  | 5062                                 | 1975.5                |
| None               | 5072                                 | 1971.5                |
| p-Cl               | 5075                                 | 1970.5                |
| m-Cl               | 5082                                 | 1968.0                |
| m-NO <sub>2</sub>  | 5095                                 | 1963.0                |
| o-OCH <sub>3</sub> | 5057                                 | 1977.5                |
| o-Cl               | 5072                                 | 1971.5                |
| o-NO <sub>2</sub>  | 5084                                 | 1967.0                |

### 8.3.1 Combinations

The band near 5070 cm<sup>-1</sup> (1972 nm) is due to a combination of NH stretching and bending. A number of examples of band positions are included in Table 8.3.

## 8.4 Ammonia

Ammonia, being a weak base, is primarily in the form of NH<sub>3</sub> in water, and its spectrum resembles that of an amine. Ammonia in water shows strong bands at 6520 cm<sup>-1</sup> (1534 nm), 5000 cm<sup>-1</sup> (2000 nm), and 4525 cm<sup>-1</sup> (2210 nm) in addition to water bands.<sup>12</sup> See Figure 8.2. The first overtone near 6520 cm<sup>-1</sup> appears as a single peak, even in gaseous ammonia.<sup>13</sup> In fact, gaseous ammonia has been recommended as a wavelength standard for NIR spectrometers. In a 10 cm cell, bands at 6609 cm<sup>-1</sup>



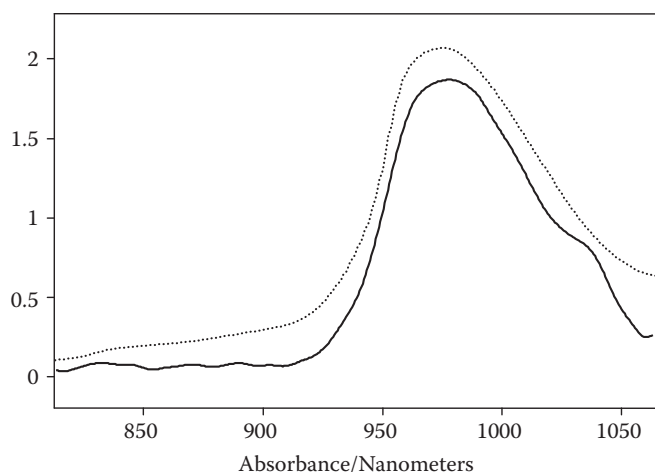
**FIGURE 8.3** NIR spectrum of ammonia in water (bottom) compared to water itself (top). Note: The top curve is 5% ammonium hydroxide in water. The dotted curve is pure water, and the bottom curve shows the difference between the two, slightly expanded to accentuate the peaks.

(1513 nm), 5084 cm<sup>-1</sup> (1967 nm), and 4417 cm<sup>-1</sup> (2264 nm) were cited.

There is also a sharp second overtone peak at about 9560 cm<sup>-1</sup> (1046 nm), as shown in Figure 8.3.<sup>14</sup>

## 8.5 Aliphatic and Aromatic Amides: Overtones

NIR spectra of primary amides (RCO-NH<sub>2</sub>), such as formamide, acetamide, and benzamide, have been studied in chloroform solution.<sup>15</sup> Two bands at 6710 cm<sup>-1</sup>



**FIGURE 8.4** Low wavelength region of 10% ammonia in water (solid curve) compared to water (dotted curve).

(1490 nm) and  $6995\text{ cm}^{-1}$  (1430 nm) have been assigned to first overtones of the asymmetric and symmetric N-H stretching modes.

The assignment of secondary amides has also been studied extensively. A single band between  $6711$  and  $6803\text{ cm}^{-1}$  (1470 to 1490 nm) for N-methylacetamide and other simple amides was attributed to the first overtone NH stretch. Dilute solutions of N-methylacetamide in either carbon tetrachloride or water have a band at  $6711\text{ cm}^{-1}$  (1470 nm), whereas more concentrated solutions have a doublet in the  $6666$ – $6880\text{ cm}^{-1}$  (1500–1700 nm) range.<sup>16</sup> In  $\text{CCl}_4$ , the bonded doublet appears at concentrations above 1 M,

whereas in water the unassociated band is present until about 8 M.

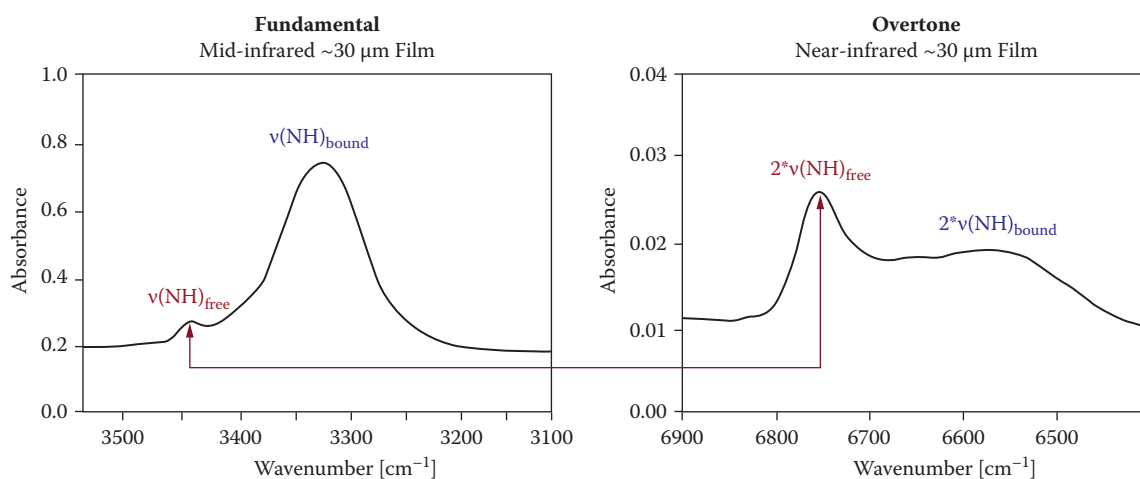
When the fundamental and first overtone NH stretch absorptions of secondary amides are compared, it is observed that the relative intensities of the free and bound peaks are very different. As seen in Figure 8.5, the overtone of the “free” NH is relatively stronger in the first overtone when compared to the fundamental. This is because hydrogen bonding has increased the anharmonicity of the vibration resulting in the higher intensity overtone.

As in amines, the first overtone of OH and NH stretching absorptions are comparable in intensity, whereas in the fundamental region the OH is much stronger. A comparison of OH and NH first overtone peak intensities can be seen in Figure 8.6. The figure illustrates the reaction of phenol with an isocyanate to form an amide.

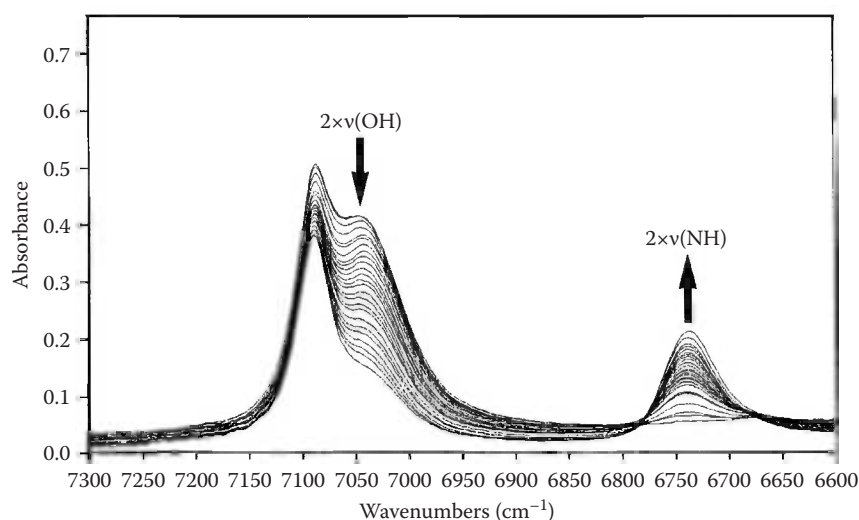
The second overtone of primary amides occurs at  $10110$ – $10260\text{ cm}^{-1}$  (975 to 989 nm). The second overtone of secondary amides is near  $10194\text{ cm}^{-1}$  (981 nm).

### 8.5.1 Amides: Combinations

In primary amides, a single combination band of symmetric and asymmetric NH stretching appears at  $6805\text{ cm}^{-1}$  (1470 nm). Several bands near  $5100$  and  $4925\text{ cm}^{-1}$  (1960 and 2030 nm) have been assigned to the combinations of NH stretch and amide II and III deformations (these mid-IR bands are generally considered to be due to different types of coupling of the CNH deformation



**FIGURE 8.5** The effect of hydrogen bonding on the anharmonicity and NH first overtone intensity in an aliphatic polyamide. (From Siesler, H. W., Ozaki, Y., Kawata, S., Heise, H. M., *Near-Infrared Spectroscopy*, Wiley-VCH, Weinheim, 2002. With permission.)



**FIGURE 8.6** Hydroxyl first overtone peak decrease and amide NH peak increase during a reaction. (From Dittmar, K., Siesler, H. W., Fresenius J. Anal. Chem. 1998, 362, 111. With permission.)

**Table 8.4 Summary of Urea Absorptions**

| Band Assignment  | Wavenumber (cm <sup>-1</sup> ) | Wavelength (nm) |
|--|--------------------------------|-----------------|
| <b>Mid-IR Fundamental Bands</b>                                  |                                |                 |
| NH asym stretch  | 3400                           | 2941            |
| NH sym stretch   | 3300                           | 3030            |
| C=O stretch (amide I)  | 1610                           | 6211            |
| NH <sub>2</sub> deformation coupled with C-N stretch (amide II)  | 1630                           | 6135            |
| C-N stretch coupled with NH <sub>2</sub> deformation (amide III) | 1467                           | 6817            |
| NH <sub>2</sub> wagging  | 1150                           | 8696            |
| <b>NIR Bands</b>   |                                |                 |
| 1st overtone NH asym stretch                                     | 6803                           | 1470            |
| 1st overtone NH sym stretch                                      | 6736                           | 1485            |
| NH asym + NH sym   | 6666                           | 1500            |
| Asym NH stretch + Amide II                                       | 5025                           | 1990            |
| Sym NH stretch + Amide II  | 4902                           | 2040            |
| Asym NH stretch + Amide III                                      | 4808                           | 2080            |
| 2 X Amide I + Amide III  | 4687                           | 2180            |
| Asym NH stretch + NH <sub>2</sub> rocking                        | 4505                           | 2220            |

and CN stretch). For example, a strong band at 5100 cm<sup>-1</sup> (1960 nm) has been assigned to the combination of asymmetric NH stretching with amide II. Two weak bands at 4925 cm<sup>-1</sup> (2030 nm) and 4975 cm<sup>-1</sup> (2010 nm) have been

**Table 8.5 Summary of Secondary Amide Bands in Protein**

| Band Assignment               | Wavenumber | Wavelength |
|-------------------------------|------------|------------|
| 1st overtone NH               | 6250–6540  | 1530–1600  |
| NH stretch + Amide II         | 4850       | 2060       |
| 2 X C=O (Amide I) + Amide III | 4590       | 2180       |

attributed to the combination of asymmetric NH stretching with amide III and symmetric NH stretching with amide III, respectively.

The NIR spectrum of urea, a special case of primary amide, was described by Murray.<sup>12</sup> Urea and thiourea were also discussed by Bala and Ghosh.<sup>17</sup> Table 8.4 provides a summary of its overtone and combination peaks. The fundamental bands listed in the table provide background information to help explain the combinations.

For secondary amides, the combination bands in the range of 4950–5000 cm<sup>-1</sup> (2000–2020 nm) and 4695–4740 cm<sup>-1</sup> (2110–2130 nm) were assigned to the NH stretch with amide II and NH stretch with amide III, respectively.<sup>15</sup> An additional band at 4630 cm<sup>-1</sup> (2160 nm) was attributed to the combination of the first overtone of C=O with amide III (2ν<sub>C=O</sub> + amide III).<sup>18</sup>

The main combination bands of secondary amides are summarized in Table 8.5. These bands are important in the analysis of proteins. As explained by Murray in his chapter on spectral comparisons,<sup>12</sup> two of the combination

**Table 8.6 Secondary Amide Bands in Polyamide 11**

| Band Assignment                          | Wavenumber | Wavelength |
|--|------------|------------|
| 1st overtone nonbonded NH                | 6760       | 1480       |
| 1st overtone bonded NH, disordered phase | 6600       | 1515       |
| 1st overtone bonded NH, ordered phase    | 6500       | 1538       |
| Bonded NH + 2 x Amide II                 | 6368       | 1570       |
| Amide I + 3 x Amide II                   | 6256       | 1598       |
| 4 x Amide II                             | 6180       | 1618       |
| Bonded NH + Amide I                      | 4970       | 2012       |
| Bonded NH + Amide II                     | 4870       | 2053       |
| 2 x Amide II + Amide I                   | 4701       | 2127       |
| Bonded NH + Amide III                    | 4586       | 2183       |
| 2 x Amide I + Amide III                  | 4521       | 2212       |

Note: See Table 8.4 for explanation of nomenclature.

**Table 8.7 Unassociated Amides Peaks for Gamma-Valerolactam in CCl<sub>4</sub>**

| Assignment                    | Wavenumber (cm <sup>-1</sup> ) | Wavelength (nm) |
|-------------------------------|--------------------------------|-----------------|
| NH stretch + NH bending       | 4865                           | 2055            |
| NH stretch + Amide II         | 4785                           | 2090            |
| NH stretch + Amide III        | 4715                           | 2120            |
| 2 x C=O (Amide I) + Amide III | 4660                           | 2145            |

bands of proteins lie on either side of the OH combination band of carbohydrates. Therefore, the shape of the spectral region near 4760 cm<sup>-1</sup> (2100 nm) is indicative of the relative amounts of protein and carbohydrate in food and agricultural products. Secondary amide peaks are also important in the analysis of nylon and many pharmaceuticals.

Wu and Siesler have assigned additional secondary amide bands in their study of the aliphatic polymer polyamide 11 (PA11).<sup>19</sup> Using deuteration, variable temperature, and polarization measurements, the assignments listed in Table 8.6 were made.

The tertiary amides lack the NH absorptions observed in the primary and secondary amides. A band at 4675 cm<sup>-1</sup> (2139 nm) for N,N-dimethylformamide, at 4650 cm<sup>-1</sup> (2151 nm) for N,N-dimethylacetamide, and at 4630 cm<sup>-1</sup> (2160 nm) for N,N-dimethylbenzamide corresponds to the combination band of 2ν<sub>C=O</sub> + amide III.

## 8.6 Amides: Cyclic (Lactams)

NIR spectra of lactams primarily show bands attributable to nonhydrogen bonded amides.<sup>20</sup> This is in contrast to linear secondary amides, which do show hydrogen-bonded peaks. The NIR region provides a means of distinguishing cis (cyclic) and trans (linear) amides, especially for hydrogen-bonding studies. Table 8.7 summarizes the band assignments for the unassociated lactam amide bands.

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# Chapter 9

## **P-H and S-H**

## 9.1 P-H

The first overtone of P-H stretching was found at  $5288\text{ cm}^{-1}$  (1891 nm) in a number of organophosphorus compounds. It is slightly more intense than the S-H absorption, having a molar absorptivity of about  $0.24\text{ L/mole-cm}$ . It is described as being more diffuse and less sharp, however.<sup>1</sup>

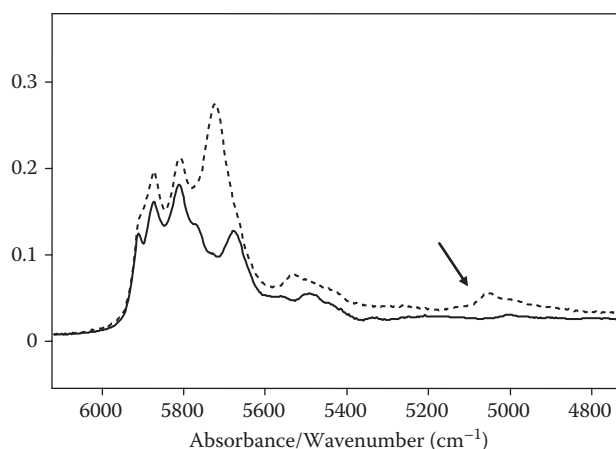
The POH group is observed in phosphorothioic acids. The absorption is significantly shifted relative to the hydroxyl in alcohols, as it is in the mid-infrared. The near-infrared peak appears at about  $5241\text{ cm}^{-1}$  (1908 nm).

## 9.2 S-H

Goddu mentions a weak S-H first overtone band for benzenethiol and 1-butanethiol at  $5076\text{--}5051\text{ cm}^{-1}$  (1970 to 1980 nm).<sup>2</sup> He cites molar absorptivities of 0.081 and  $0.044\text{ l/mole-cm}$ , respectively. This band is probably a non-bonded S-H. It is also weak in the mid-infrared, although strong in the Raman. Although a bonded S-H would be broader and placed at a lower wavenumber (higher wavelength), Williams has indicated that the S-H is not as amenable to hydrogen bonding as the O-H is. Liquid thiols (mercaptans) have sharper peaks than liquid alcohols.<sup>3</sup>

The first overtone of the S-H group can be seen in Figure 9.1 as the weak peak near  $5050\text{ cm}^{-1}$ .

The phosphorus-thiol group (P-SH) shows a shift from the normal thiol overtone and gives rise to a weak doublet at  $5076\text{--}5002\text{ cm}^{-1}$  (1970 and 1999 nm).<sup>4</sup>



**FIGURE 9.1** The S-H first overtone (dotted curve), shown in butane thiol and compared to pentane (solid curve).

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# Chapter 10

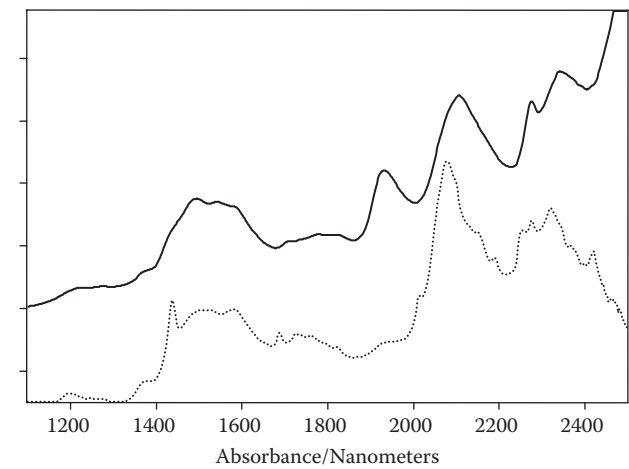
## **Carbohydrates**

10.1 Introduction

Carbohydrates include saccharides and polysaccharides or sugars and starches and cellulosic or lignin-type biomolecules. They consist mostly of aliphatic cyclic groups with attached OH groups and ether linkages. Lignin is representative of aromatic natural product compounds. Thus the bands normally associated with these functional groups may be observed in the near-infrared (NIR) spectra of carbohydrate molecules.

Table 10.1 is a useful reference indicating the appearance of bands related to starches and sugars. Figure 10.1 shows two of these classic spectra, cornstarch and sucrose.

| Table 10.1 Bands Associated with Starches and Sugars as C-H and O-H Related Bands |              |                          |
|---|--------------|--------------------------|
| Functional Grouping   | Nanometers   | Wavenumbers              |
| C-H stretching & C-C & C-O-C stretching combination                               | 2500         | 4000                     |
| C-H stretching & CH <sub>2</sub> deformation combination                          | 2280–2330    | 4283–4386                |
| O-H bending & C-O stretching combination<br>O-H/C-O<br>Polymeric (.O-H & .C-O)    | 2100         | 4762                     |
| O-H (2v), .O-H -O-H<br>Polymeric (.O-H)   | 1450         | 6897                     |
| 3vO-H, saccharides  | 1009 and 972 | 9911 and 10288 (doublet) |



**FIGURE 10.1** Powdered corn starch (solid curve) and crystalline sucrose (dotted curve).

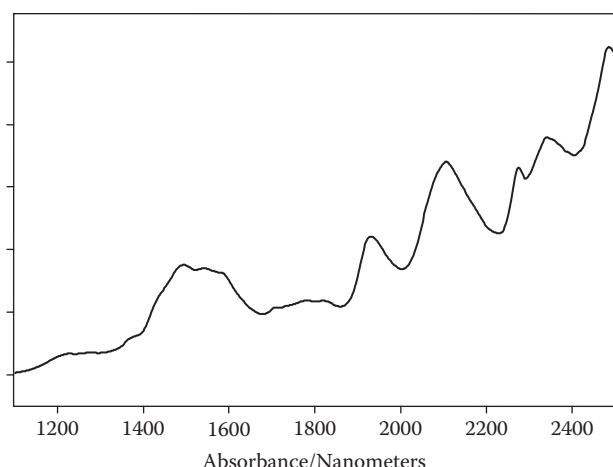
Note the sharp nonbonded OH peak near 1430 nm and the lack of a water peak near 1940 nm in sucrose.

10.2 Cellulose and Cellulosic Compounds

An excellent reference article for background reading is supplied by Blackwell.<sup>1</sup> The article reviews the work in infrared and Raman spectroscopy of cellulosic materials up to 1977, including a detailed table giving calculated and observed band assignments for cellulose I. Table 10.2 shows observed band positions for cellulose I functional groups with corresponding first and second overtone positions between 996 nm and 2500 nm (9091 to 4000 cm<sup>-1</sup>) and Figure 10.2 shows its spectrum. Bands thought to associate with fiber parameters such as cellulose and lignin are presented in Table 10.3 and Table 10.4, respectively. Multiple quantitative calibrations have demonstrated that cellulose and lignin are determined using the regions from 4348 to 4237 cm<sup>-1</sup> (2300 to 2360 nm) and 6042 to 5865 cm<sup>-1</sup> (1655 to 1715 nm).<sup>2</sup>

Wingfield<sup>3</sup> discussed the possibilities for NIR detection of cellulose in flour. He summarizes work up until the publication and cites early workers in the field. Marton and Sparks<sup>4</sup> have reported measurements of lignocellulose in the infrared region by using simple linear regression

| Table 10.2 Cellulose I Associated Bands  |            |             |
|--|------------|-------------|
| Functional Grouping  | Nanometers | Wavenumbers |
| C-H stretching & C-C & C-O-C stretching combination                            | 2500       | 4000        |
| C-H stretching & C-C stretching combination                                    | 2488       | 4019        |
| 3 X (.C-H bending): C-H  | 2352       | 4252        |
| C-H (2v CH <sub>2</sub> symmetric stretching & δ CH <sub>2</sub> ) combination | 2347       | 4261        |
| C-H stretching & CH <sub>2</sub> deformation combination                       | 2280–2330  | 4283–4386   |
| O-H/C-H Cellulose  | 2270       | 4405        |
| O-H Polymeric O-H (2v)   | 2090       | 4785        |
| O-H stretching & C-O stretching (3v) combination                               | 1820       | 5495        |
| C-H Methylene (2vC-H)  | 1780       | 5618        |
| O-H Polymeric (2vO-H)  | 1450       | 6897        |
| O-H (3v)   | 996        | 10040       |



**FIGURE 10.2** Powdered crystalline cellulose reflection spectrum.

of lignin content versus the absorbance ratio of 1510/1310  $\text{cm}^{-1}$ ; these frequencies correspond to a ratio of second overtones occurring near 4529/3929  $\text{cm}^{-1}$  (2208/2545 nm). Lignin exhibits the strong presence of many aromatic rings and associated functional groups (see Table 10.4).

Gould et al.<sup>5</sup> reported using an infrared frequency shift of the 2900  $\text{cm}^{-1}$  band (3448 nm), which would correspond

to a frequency shift at a first overtone band near 5800  $\text{cm}^{-1}$  (1724 nm). Mitchell and coworkers<sup>7</sup> determined acetyl content of cellulose acetate using NIR from 35% to 44.8% acetyl. The spectra were measured in 5 cm cells against a reference solution of pyrrole containing 5% carbon tetrachloride. The maximum absorbance at 6920  $\text{cm}^{-1}$  (1445 nm) was plotted against percent acetyl to obtain a calibration line. A standard deviation of 0.22% was indicated by the NIR method. NIR spectroscopy was evaluated for monitoring the acid-catalyzed hydrolysis (thinning) of starch (I) using a univariate calibration model based on the integrated area of the 4400  $\text{cm}^{-1}$  (2272 nm) absorption band for carbohydrates.<sup>8</sup>

### 10.3 Glucose in Aqueous Solution

Glucose has been analyzed in blood and saline for medical applications using NIR with recent developments in chemometric approaches to overcome interference issues and type II errors (false negative outliers) in the presence of other saccharides normally found in blood from both endogenous and exogenous sources.<sup>8,9</sup>

**Table 10.3** Bands Normally Associated with “Fiber” as Cellulosics

| Functional Grouping  | Nanometers | Wavenumbers |
|--|------------|-------------|
| C-H stretching + C-C stretching combination                                      | 2488       | 4019        |
| C-H bending  | 2352       | 4252        |
| C-H ( $2\nu\text{CH}_2$ symmetric stretching + $\delta\text{CH}_2$ ) combination | 2347       | 4261        |
| C-H stretching plus $\text{CH}_2$ deformation combination                        | 2335       | 4283        |
| O-H stretching plus $2 \times \text{C-O}$ stretching combination                 | 1820       | 5495        |
| $\text{CH}_2$ : stretching ( $2\nu$ )  | 1780       | 5618        |
| O-H Polymeric (.O-H): O-H ( $2\nu_s$ ), .O-H                                     | 1490       | 6711        |
| O-H ( $3\nu$ ) ( $-\text{CH}_2\text{-OH}$ )                                      | 996        | 10040       |

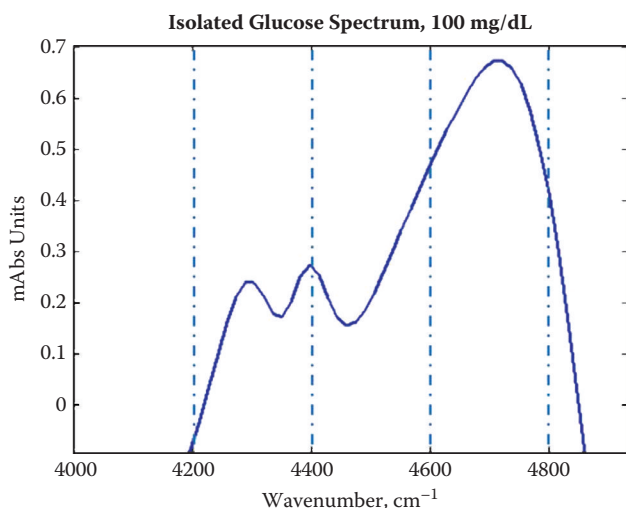
**Table 10.4** Bands Normally Associated with “Fiber” as Lignins

| Functional Grouping  | Nanometers | Wavenumbers |
|--|------------|-------------|
| $\text{CC}\omega + \text{CH}\nu$ (11+ 12), Aromatic ring band assignment   | 2540       | 3937 (3935) |
| C-H stretching + $\text{C=O}$ combination  | 2200       | 4545        |
| C-H ( $2\nu$ ), ArC-H: C-H Aromatic associated C-H   | 1685       | 5935        |
| C-H ( $2\nu\text{CH}_2 + \delta\text{CH}_2$ ) combination: C-H Methylene C-H, associated with linear aliphatic $\text{R}(\text{CH}_2)_N\text{R}$ | 1410       | 7092        |
| C-H combination, Aromatic associated C-H   | 1417       | 7057        |
| C-H ( $3\nu$ ), .HC=CH   | 1170       | 8547        |
| C-H ( $4\nu$ ), Aromatic associated C-H  | 876        | 11655       |

**Table 10.5 Optical Near Infrared Absorption Bands Associated with Glucose and Saccharide Molecular Structures**

| Functional Grouping                      | Spectra–Structure Correlation   | Nanometers | Wavenumbers |
|--|---|------------|-------------|
| C=O-O Polymeric (C=O and C-O stretching) | C=O-O (4v)  | 2100       | 4762        |
| O-H/C-O Polymeric (.O-H + .C-O)          | O-H bending & C-O stretching combination                                    | 2100       | 4762        |
| O-H/C-O from glucose                     | O-H/C-O Glucose absorption from O-H stretching & C-O stretching combination | 2273       | 4400        |
| C-H Starch (.C-H + CH <sub>2</sub> )     | C-H stretching & CH <sub>2</sub> deformation                                | 2280       | 4386        |
| C-H (.C-H + CH <sub>2</sub> )            | C-H stretching & CH <sub>2</sub> deformation combination                    | 2322       | 4307        |
| C-H (.C-H + CH <sub>2</sub> )            | C-H stretching & CH <sub>2</sub> deformation combination                    | 2330       | 4292        |
| C-H (.C-H + CH <sub>2</sub> )            | C-H stretching & CH <sub>2</sub> deformation combination                    | 2335       | 4283        |
| C-H (.C-H bending)                       | C-H (3δ)  | 2352       | 4252        |

Source: Workman, J., Abookasis, D. Traps and pitfalls when applying chemometrics to biomedical problems, Federation of Analytical Chemistry and Spectroscopy Societies, **Pittsburgh Conference, Atlanta, 2011.**



**FIGURE 10.3** Glucose in saline spectral bands: glucose in 0.9% saline (100 mg/dL) with saline spectrally subtracted (vector difference) showing the predominant glucose related bands, with spectra-structure correlations indicated in Table 10.5 (1 mm path length).

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# Chapter 11

## **Amino Acids, Peptides, and Proteins**

## 11.1 Proteins

Protein is measured in the near-infrared (NIR) region as its associated functional groups, such as amides and various C-H functional groups. For example, key band locations associated with proteins are found at 10277 to 9804  $\text{cm}^{-1}$  (973 nm to 1020 nm) as N-H stretch second overtone; 6667 to 6536  $\text{cm}^{-1}$  (1500 nm to 1530 nm) as N-H stretching first overtone; and 4878 to 4854  $\text{cm}^{-1}$  (2050 nm to 2060 nm) representing N-H stretching combinations. The 4613 to 4587  $\text{cm}^{-1}$  (2168 nm to 2180 nm) region is associated with the N-H bend second overtone and C=O stretch–N-H in-plane bending–C-N stretch combination bands. See Chapter 8 for a more complete description of amide bands.

Hermans and Scheraga<sup>1</sup> made measurements of the backbone peptide hydrogen-bond system (NH group) using NIR measurements in the extended spectral region from 14286 to 2857  $\text{cm}^{-1}$  (700–3500 nm). The authors describe the use of NIR to distinguish between hydrogen-bonded and nonhydrogen bonded N-H and O-H groups. Molecules examined include methanol, aniline, and poly-g-benzyl-L-glutamate.

Elliott and Ambrose<sup>2</sup> identify absorption bands for polypeptides and proteins at approximately 3505  $\text{cm}^{-1}$  (2853 nm) as N-H associated stretching bands and 4825  $\text{cm}^{-1}$  (2073 nm) in the overtone region. The main result of their work was to demonstrate that a band at 4840  $\text{cm}^{-1}$  (2066 nm) is useful for distinguishing the presence of extended versus folded configurations for polypeptides and proteins, even in the presence of liquid phase water. The band near 4824  $\text{cm}^{-1}$  (2073 nm) was classified earlier by Glatt and Ellis<sup>3</sup> on work in nylon as a combination band of the N-H deformation and stretching modes.

Hecht and Wood<sup>4</sup> describe in a detailed study the band assignments for peptides. The authors identify the bands for a porcupine quill spectrum as shown in Table 11.1.

A summary of all bands thought to be associated with protein as amides is presented in Table 11.2. Multiple quantitative calibrations for protein in the agricultural literature demonstrate the area from 4655 to 4545  $\text{cm}^{-1}$  (2148 nm to 2200 nm) as used for protein determination.<sup>5</sup>

Fraser and MacRae<sup>6</sup> have reported important absorption bands for natural product proteins and nylon polyamide at 4870  $\text{cm}^{-1}$  (2188 nm) resulting from a combination of the peptide absorptions at 3305  $\text{cm}^{-1}$  (3026 nm), and 1540  $\text{cm}^{-1}$  (6494 nm). For feather shafts, the authors report absorption bands at 4970  $\text{cm}^{-1}$  (2012 nm) and 5040  $\text{cm}^{-1}$  (1984 nm). A shoulder at 5040  $\text{cm}^{-1}$  (1984 nm) was reported as resulting from side chain amide groups. For beta-keratin, the paper reports important absorption bands at 4600  $\text{cm}^{-1}$  (2174 nm), 4850  $\text{cm}^{-1}$  (2062 nm), and 4970  $\text{cm}^{-1}$  (2012 nm). The authors were interested in studying the amorphous components of naturally occurring protein structures.

## 11.2 Protein Structure

The most pronounced changes for the thermal unfolding of ribonuclease (RNase) A are observed from 4820 to 4940  $\text{cm}^{-1}$ . The strong N-H combination band found at 4867  $\text{cm}^{-1}$  in the spectrum of native RNase A shifts to 4878  $\text{cm}^{-1}$  upon thermal unfolding. The thermal unfolding of RNase A begins with some changes in  $\beta$ -sheet structure, followed by the loss of  $\alpha$ -helical structures, and then ending with the unfolding of the remaining  $\beta$  sheets.<sup>7</sup> Fourier transform NIR (FT-NIR) spectra have been measured for

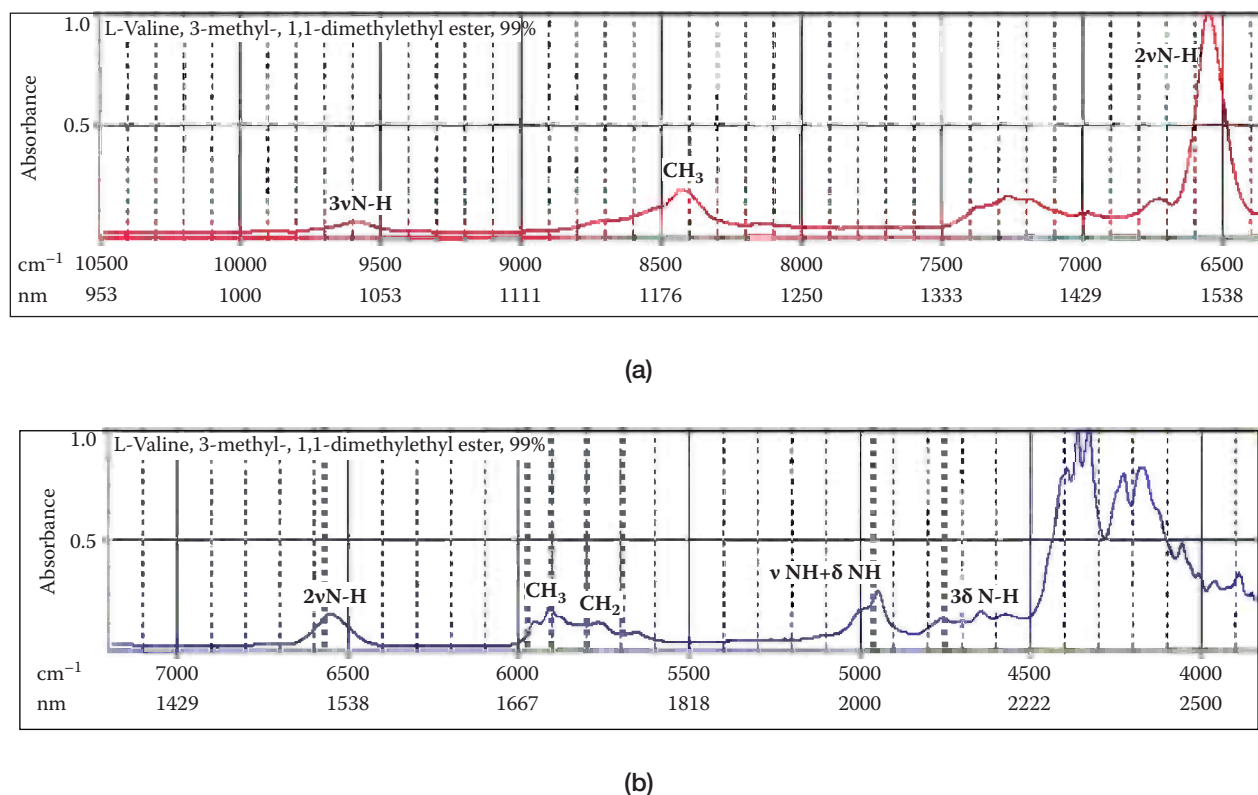
**Table 11.1 Band Assignments for Peptide Groups as Delineated by Hecht and Wood**

| Reported Band Assignments             | Wavenumber | Wavelength (nm) |
|---------------------------------------|------------|-----------------|
| C-H stretch + CH deformation          | 3950–4400  | 2532–2270       |
| 2 X stretch C=O + peptide group mode  | 4590       | 2180            |
| N-H stretch + peptide group mode      | 4850       | 2060            |
| OH stretch + OH deformation of water  | 5135       | 1947            |
| 2 X CH stretch                        | 5700–5850  | 1750–1710       |
| 2 X NH stretch                        | 6500       | 1540            |
| 2 X OH stretch + deformation of water | 6900       | 1450            |
| 3 X CH stretch                        | 8100       | 1235            |

**Table 11.2 Absorption Bands Associated with “Proteins” as Amides**

| Functional Grouping  | Nanometers | Wavenumbers |
|--|------------|-------------|
| N-H/C-N/N-H [Bonded NH stretching & Amide III (C-N stretching/N-H in-plane bending) combination] from polyamide 11   | 2183       | 4586        |
| N-H (3 $\delta$ )  | 2180       | 4587        |
| N-H/C-N/C=O [2x Amide I (2 $\nu_s$ C=O stretching) & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea                         | 2180       | 4687        |
| N-H/C-N/C=O [2x Amide I (2 $\nu_s$ C=O stretching) & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for secondary amides in proteins | 2180       | 4590        |
| N-H/C-N [ $\nu_s$ N-H asymmetric & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea   | 2080       | 4808        |
| N-H [ $\nu$ N-H & Amide II deformation (N-H in-plane bending) combination] for secondary amides in native RNase A  | 2075       | 4820        |
| N-H (3 $\delta$ ) & N-H stretching combination   | 2060       | 4854        |
| N-H [ $\nu$ N-H & Amide II deformation (N-H in-plane bending) combination] for secondary amides in proteins  | 2060       | 4850        |
| CONH <sub>2</sub> combination of amide A and amide II  | 2060       | 4855        |
| N-H stretching & C=O stretching (Amide I) combination  | 2055       | 4866        |
| N-H ( $\nu$ N-H & $\delta$ N-H combination) for Gamma-valerolactam   | 2055       | 4865        |
| N-H combination band found in the spectrum of native RNase A (C=O amide I band)  | 2055       | 4867        |
| CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures.   | 2055       | 4865        |
| N-H stretching & C=O stretching (Amide I) combination band in the spectrum of native RNase A   | 2055       | 4867        |
| N-H from CONH <sub>2</sub> as thermal unfolding of RNase A protein in aqueous solution (Assigned to an N-H combination band)                                   | 2055–2050  | 4867–4878   |
| N-H in-plane bend & C-N stretching & N-H in-plane bend combination   | 2050       | 4878        |
| N-H native RNase A combination band at 4867cm <sup>-1</sup> shifting due to thermal unfolding (C=O amide I band)   | 2050       | 4878        |
| N-H stretching & C=O stretching (Amide I) combination band observed in the thermal unfolding observed in native RNase A  | 2050       | 4878        |
| N-H [ $\nu$ N-H symmetric & Amide II deformation (N-H in-plane bending) combination] for primary amides  | 2040       | 4902        |
| C=O (3 $\nu$ ), .C=ONH <sub>2</sub>  | 2030       | 4926        |
| N-H [ $\nu$ N-H asymmetric & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for primary amides                                       | 2030       | 4925        |
| N-H/C=O [Bonded NH stretching & Amide I (2 $\nu_s$ C=O stretching) combination] of native RNase A  | 2024       | 4940        |
| N-H [ $\nu$ N-H symmetric & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for primary amides  | 2010       | 4975        |
| N-H [ $\nu$ N-H asymmetric & Amide III deformation (C-N stretching/N-H in-plane bending) combination] for primary amides                                       | 1990       | 5025        |
| N-H stretching (asymmetric) & N-H in-plane bending combination   | 1980       | 5051        |
| CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures.   | 1691–1688  | 5915–5925   |
| N-H (2 $\nu$ ), .CONHR   | 1490       | 6711        |
| N-H (2 $\nu$ ), .CONH <sub>2</sub>   | 1483       | 6743        |
| N-H (2 $\nu$ ), .CONHR   | 1471       | 6798        |
| N-H ( $\nu$ N-H asymmetric & $\nu$ N-H symmetric combination) for primary amides   | 1470       | 6805        |





**FIGURE 11.1** (a) L-Valine, 3-methyl, 1,1-dimethylethyl ester (amino acid) spectrum (952–1587 nm). (b) L-Valine, 3-methyl, 1,1-dimethylethyl ester (amino acid) spectrum (1389–2632 nm). (Spectra used by permission from *NIR Spectra of Organic Compounds*, Wiley-VCH, ISBN 3-527-31630-2.)

various polypeptides and proteins with different secondary structures in order to identify an NIR marker band for the protein and polypeptide structures. Comparison between FT-NIR and FT-mid-IR spectra has shown a correlation between the frequency of a band near 4855  $\text{cm}^{-1}$ , assignable to a combination of amide A and amide II, and that of a mid-IR band near 3300  $\text{cm}^{-1}$  assigned to amide A (N-H stretch).<sup>8</sup> The NIR spectra of various proteins (bovine serum albumin, lysozyme, ovalbumin,  $\gamma$  globulin,  $\beta$  lactoglobulin, myoglobin, cytochrome c) have been investigated for potential measurement of protein secondary structure. The spectra of proteins in aqueous solutions and as freeze-dried solids indicated  $\alpha$ -helix information present at 4090, 4365–4370, 4615, and 5755  $\text{cm}^{-1}$ ; and  $\beta$ -sheet information at 4060, 4405, 4525–4540, 4865, and 5915–5925  $\text{cm}^{-1}$ .<sup>9</sup>

Ovalbumin (OVA) has been studied in acidified, aqueous solutions using two-dimensional (2D) FT-NIR correlation spectroscopy. This technique demonstrates a significant change in bands when the molecule pH moves from 5.4 to 3.6. A band near 4265  $\text{cm}^{-1}$  assigned

to a symmetric methylene ( $\text{CH}_2$ ) stretching mode and a  $\text{CH}_2$  bending mode of side chains observed at pH 5.4 disappears completely in the synchronous spectrum at pH 3.6. A band near 4600  $\text{cm}^{-1}$  assigned to a combination of amide B (a Fermi resonance band relating to the first overtone of the carbonyl and the N-H stretch) and amide II shifts downward with significant broadening between pH 3.0 and 2.4. A broad band at around 6950  $\text{cm}^{-1}$  was assigned to free water and bound water with weak hydrogen bonds becomes very weak in the synchronous spectrum at pH 2.6, while broad auto peaks around 6450  $\text{cm}^{-1}$  suddenly appear that are due to bound water with several hydrogen bonds and the first overtone of an NH stretching mode of the amide groups of OVA.<sup>10</sup> FT-NIR spectra have been measured for several globular proteins and a band near 4525  $\text{cm}^{-1}$  seems to be highly associated with  $\beta$ -sheet structure. Low-wavenumber NIR bands from the 4500–4000  $\text{cm}^{-1}$  region were considered to reflect the amino acid composition of proteins.<sup>11</sup> Figure 11.1 shows a solid sample amino acid reflection spectrum.



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# Chapter 12

## **Synthetic Polymers**

## 12.1 Introduction

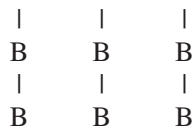
NIR spectroscopy is used in a number of applications relating to polymers. First, the technique can qualify monomers prior to polymerization reactions. Then, near infrared (NIR) can measure the kinetics of polymer onset and the detection of end-point completion and initiator compound levels in polymerization reactions. NIR spectroscopy can also be used to sort polymers and to control the quality of finished polymeric materials. Other applications include residual monomer content, copolymer or blend content, degree of cure, and crystallinity. In general, NIR spectroscopy is valuable for polymer identification, characterization, and quantification. NIR spectroscopy can be done in situ for process applications with no sample preparation and can be applied where rugged optical systems are a necessity. The low sample absorption and high energy throughput of NIR offer an advantage over the mid-IR for the analysis of polymers because thicker solid samples and longer pathlength cells for liquids are easier to work with. Some of the earliest work in applying IR and NIR spectroscopy to polymer characterization is found in references 1 to 11. Sample preparation methods are shown in reference 12.

## 12.2 Polymers

Polymers are usually large molecules consisting of repeating units or monomers. Natural polymers include starches and polysaccharides. Synthetic polymers are commonly termed *plastics* and are used for many materials and products. Polymers vary in molecular formula and molecular weight due to variation in the number of repeating units. Polymer backbone structures often have attached molecular groups. The molecular arrangement of these groups determines the stereochemical configuration for any given polymer. If all the attached groups are in the identical position along the polymer backbone chain, the polymer is in an *isotactic* configuration. If the attached groups alternate in their attached positions with a regular pattern the *syndiotactic* configuration is ascribed. When attached groups are randomly attached to the polymer backbone the polymer is said to have an *atactic* configuration. The isotactic configuration represents the most crystalline (rigid) of the configuration types.

Copolymers are formed when two or more monomer types are incorporated into a single backbone structure to

achieve specific material performance properties. Structures are classified as *alternating* (-A-B-A-B-A-B-), *random* (-A-A-B-A-B-B-A-), *block* (-A-A-B-B-B-B-A-A-), and *graft* (-A-A-A-A-A-A-A-A-).

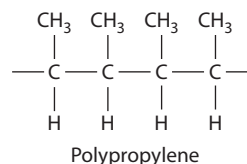


Polymerization involves the reaction of the monomer building blocks into polymers. The polymerization reaction types involve *addition* reactions and *condensation* reactions. An example addition reaction would be employing ethene to form polyethylene. Condensation reactions typically involve different reaction products reacting to form a heteropolymer and a small molecular by-product. The reaction of 1,6-diaminohexane and hexanedioic acid to form nylon and water is a classic example. Polymers made from one monomer type are termed *homopolymers*, and those formed with two different monomers are referred to as *copolymers*.

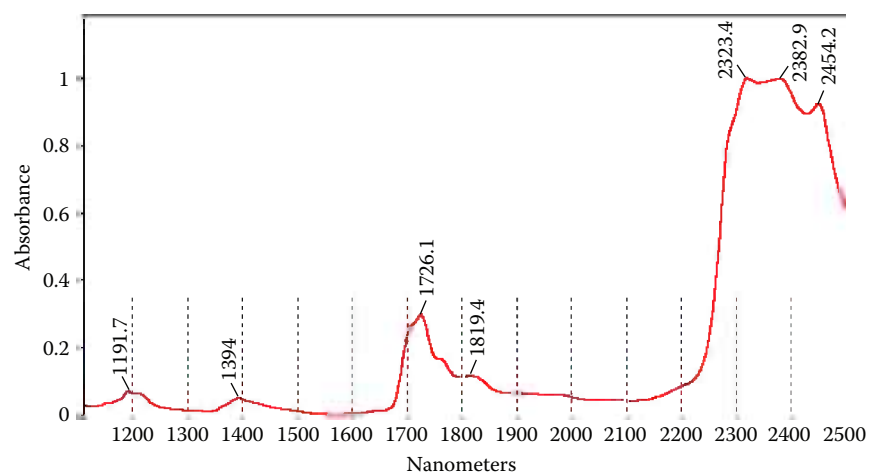
A few example polymers are shown in Figures 12.1 to 12.6. Typical polymer spectra exhibit similar NIR bands and positions that are represented by [Table 12.1](#).

## 12.3 Elastomers

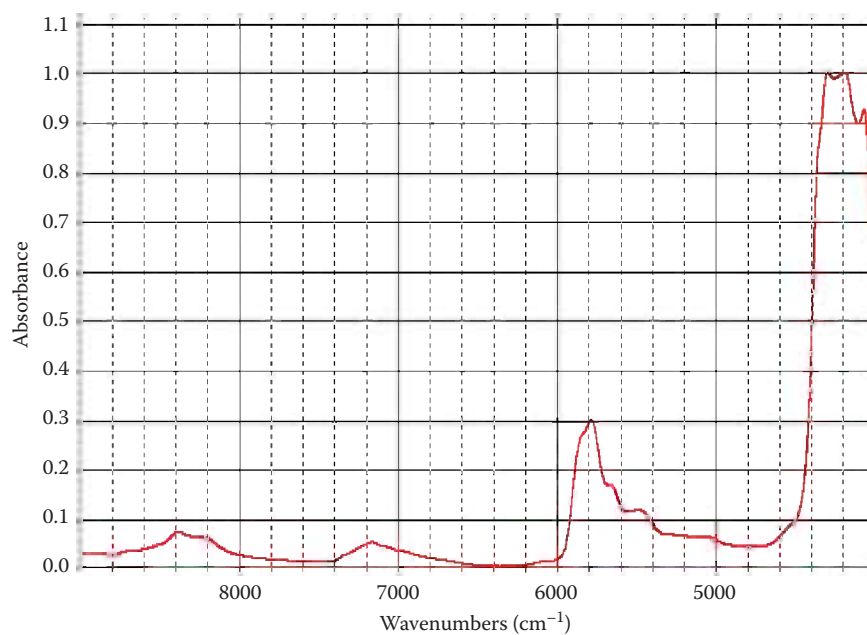
Elastomers are natural or synthetic materials having the ability to undergo deformation under the influence of an applied force and regain its original shape once the applied force is removed. Natural rubbers are polymeric materials originally obtained from the rubber tree (*Hevea brasiliensis*). The sap of this tree is a latex material that is processed by coagulation and drying the sap, and then vulcanizing and adding filler compounds. The basic natural rubber compound is isoprene, which contains the repeating unit of  $-\text{CH}_2\text{C}(\text{CH}_3):\text{CHCH}_2-$ . Synthetic rubbers exist such as nitriles, butadienes, neoprene, butyl rubbers, polysulfide rubbers, PVC, and silicone rubbers whose



**FIGURE 12.1** Polypropylene is a polyolefin comprised of repeating olefin monomer units.

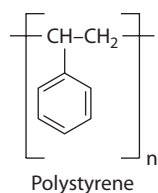


(a)



(b)

**FIGURE 12.2** (a) A NIR wavelength reflection spectrum of atactic poly(propylene) at low resolution ( $32\text{ cm}^{-1}$ ). (b) A NIR wavenumber reflection spectrum of atactic poly(propylene) at low resolution ( $32\text{ cm}^{-1}$ ).

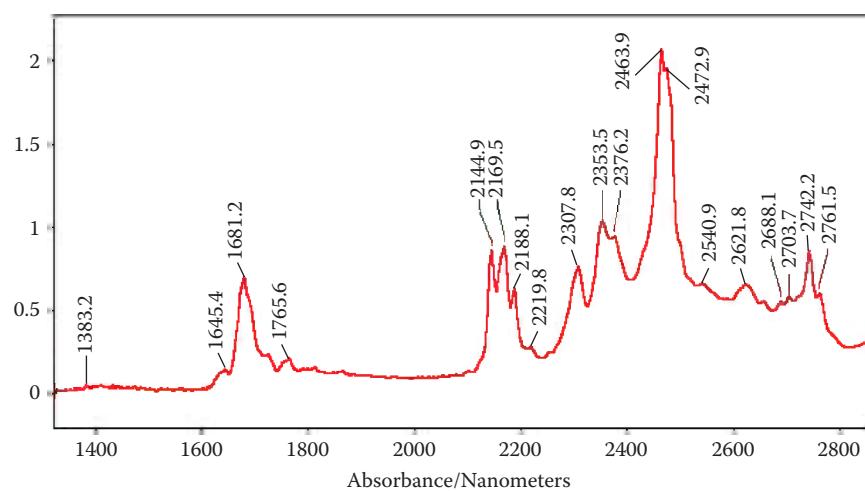


**FIGURE 12.3** Structure of styrene monomer units found in polystyrene.

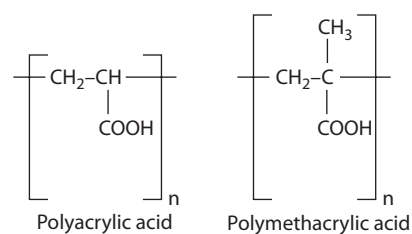
structures and NIR spectra are shown in Figures 12.7 to 12.10. Typical rubber spectra exhibit similar NIR bands and positions that are represented in [Table 12.2](#).

## 12.4 Epoxy Resins

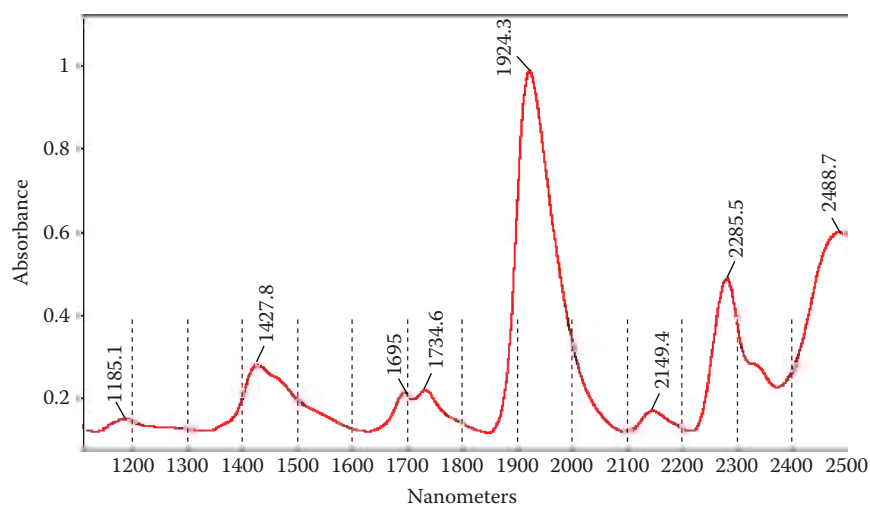
Near-infrared spectroscopy has been used extensively to follow the reaction kinetics of a variety of epoxy/amine



**FIGURE 12.4** Near-infrared reflection spectrum of crystalline poly(styrene) at  $16\text{ cm}^{-1}$  resolution.

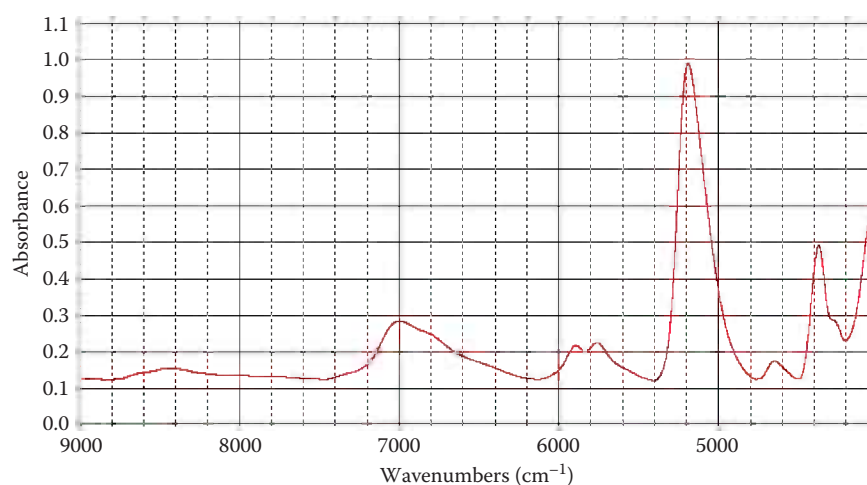


**FIGURE 12.5** Two examples of water-soluble polyacrylates.



(a)

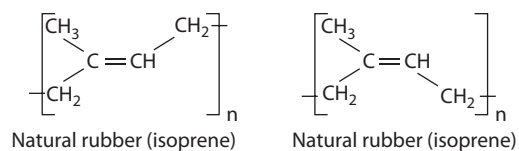
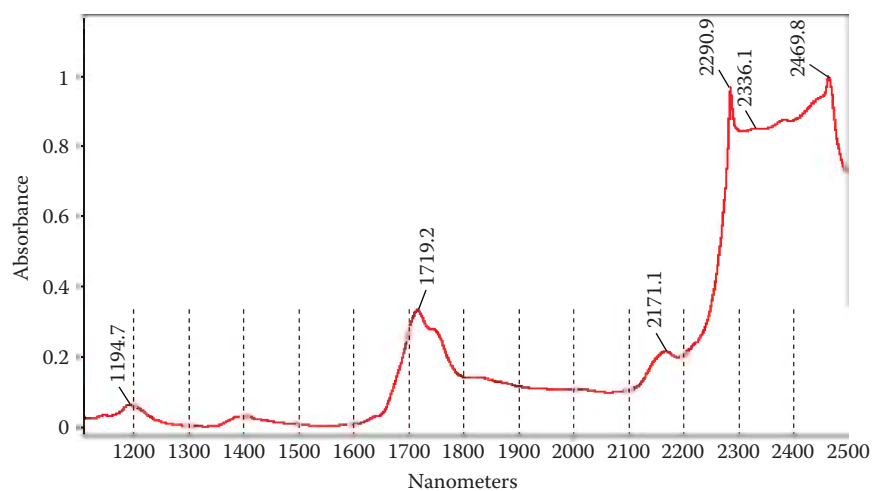
**FIGURE 12.6** (a) NIR wavelength reflection spectrum of poly(acrylic acid) at  $32\text{ cm}^{-1}$  resolution.



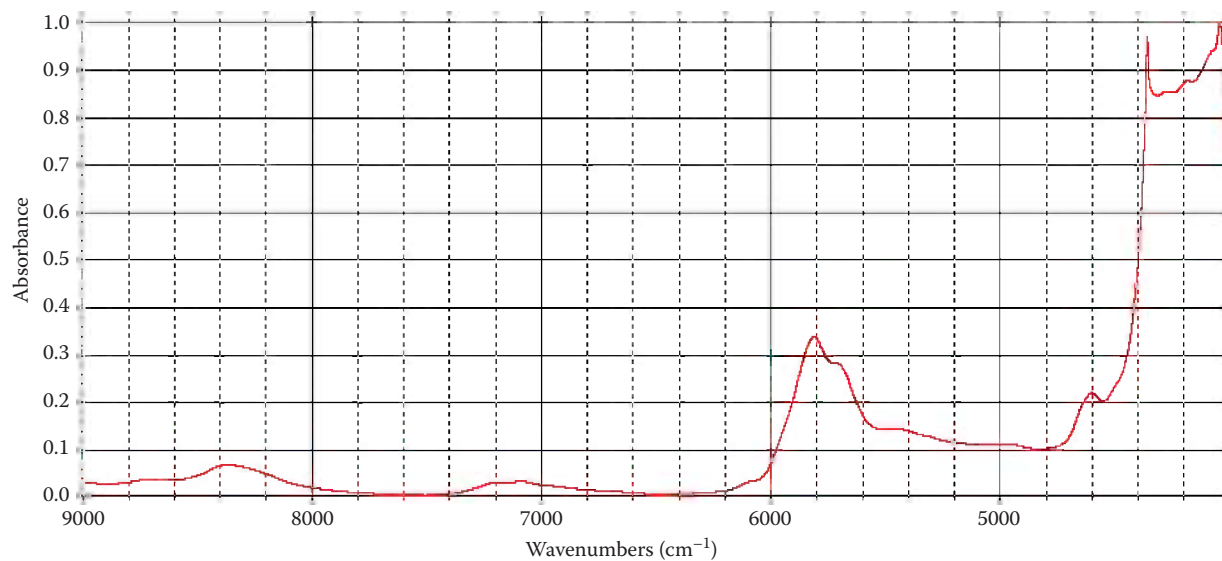
(b)

**FIGURE 12.6 (continued)** (b) NIR wavenumber reflection spectrum of poly(acrylic acid) at 32 cm<sup>-1</sup> resolution.**Table 12.1 Spectral Correlation Chart for Example Polymers**

| Polymer            | Band Locations                  | Band Assignment  |
|--------------------|---------------------------------|--|
| Poly(propylene)    | 9930 cm <sup>-1</sup> (1192 nm) | Asymmetric methyl (C-H) stretch - (3v) 2nd overtone  |
|                    | 8197 cm <sup>-1</sup> (1220 nm) | Asymmetric methylene (C-H) stretch - (3v) 2nd overtone   |
|                    | 7174 cm <sup>-1</sup> (1394 nm) | Methyl and methylene (C-H) combination   |
|                    | 5882 cm <sup>-1</sup> (1700 nm) | Asymmetric methyl (C-H) stretch - (2v) 1st overtone  |
|                    | 5794 cm <sup>-1</sup> (1726 nm) | Asymmetric methylene (C-H) stretch - (2v) 1st overtone   |
|                    | 5495 cm <sup>-1</sup> (1820 nm) | Symmetric methyl (C-H) stretch - (2v) 1st overtone   |
|                    | 4305 cm <sup>-1</sup> (2323 nm) | C-H bend - (3δ) 2nd overtone   |
|                    | 4196 cm <sup>-1</sup> (2383 nm) | C-H stretch and C-C stretching combination   |
|                    | 4075 cm <sup>-1</sup> (2454 nm) | C-H combination band   |
| Poly(styrene)      | 8757 cm <sup>-1</sup> (1142 nm) | Aromatic C-H stretch - (3v) 2nd overtone   |
|                    | 5938 cm <sup>-1</sup> (1684 nm) | Aromatic C-H stretch - (2v) 1st overtone   |
|                    | 4606 cm <sup>-1</sup> (2170 nm) | Aromatic C-H combinations  |
| Poly(acrylic acid) | 8439 cm <sup>-1</sup> (1185 nm) | Asymmetric methylene (C-H) stretch - (3v) 2nd overtone   |
|                    | 7003 cm <sup>-1</sup> (1428 nm) | O-H stretch - (2v) 1st overtone  |
|                    | 5900 cm <sup>-1</sup> (1695 nm) | Asymmetric methyl (C-H) stretch - (2v) 1st overtone  |
|                    | 5764 cm <sup>-1</sup> (1735 nm) | Asymmetric methylene (C-H) stretch - (2v) 1st overtone   |
|                    | 5198 cm <sup>-1</sup> (1924 nm) | O-H stretch - (2v) 1st overtone + C=O stretch - (2v) 2nd overtone + O-H stretch/HOH deformation combination + O-H bend (3δ) 2nd overtone |
|                    | 4653 cm <sup>-1</sup> (2149 nm) | C-H stretch/C=O stretch combination + symmetric C-H deformation  |
|                    | 4374 cm <sup>-1</sup> (2286 nm) | C-H stretch + CH <sub>2</sub> deformation + C-H bend - (3δ) 2nd overtone   |
|                    | 4018 cm <sup>-1</sup> (2489 nm) | C-H stretch + C-C stretch + C-O-C stretch combination  |

**FIGURE 12.7** Typical repeating units found in natural rubbers (trans- and cis-forms).

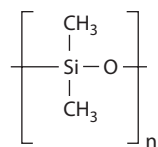
(a)



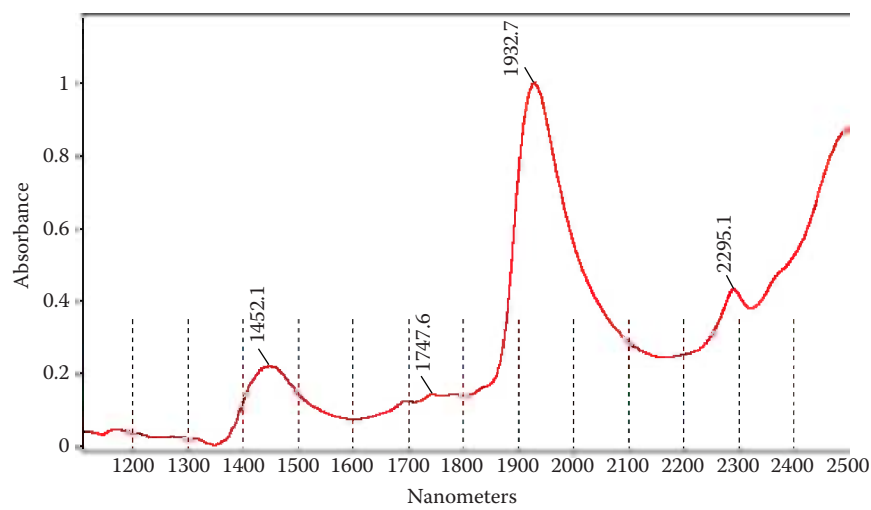
(b)

**FIGURE 12.8** (a) NIR wavelength reflection spectrum of styrene-isoprene-styrene at (32 cm<sup>-1</sup>) resolution. (b) NIR wavenumber reflection spectrum of styrene-isoprene-styrene at (32 cm<sup>-1</sup>) resolution.

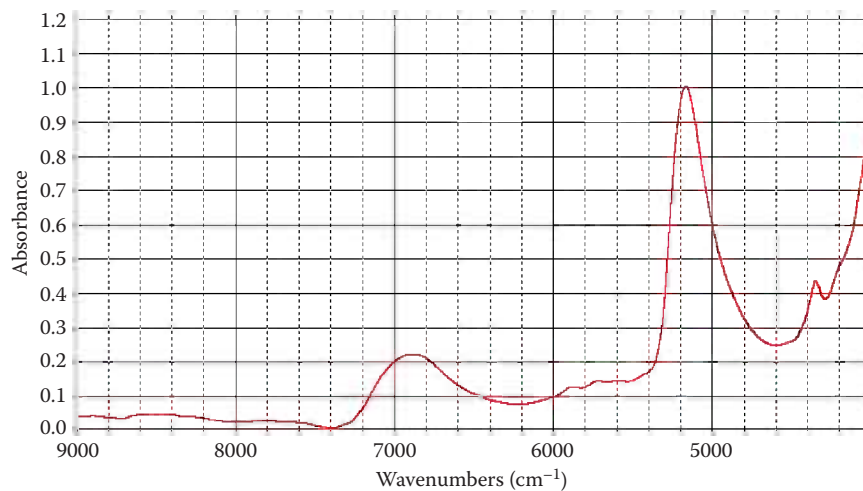




**FIGURE 12.9** Silicone rubbers (polysiloxane). Note: The alkyl group is often substituted with a variety of different groups.



(a)



(b)

**FIGURE 12.10** (a) NIR wavelength reflection spectrum of silicone (DMS) at low (32 cm⁻¹) resolution. (b) NIR wave-number reflection spectrum of silicone (DMS) at low (32 cm⁻¹) resolution.

**Table 12.2 Spectral Correlation Charts for Model Rubber Compounds**

| Rubber                       | Band Location                   | Description   |
|------------------------------|---------------------------------|---|
| Styrene-isoprene-styrene     | 8368 cm <sup>-1</sup> (1195 nm) | Methyl (C-H) stretch - (3v) 2nd overtone  |
|                              | 7143 cm <sup>-1</sup> (1400 nm) | C-H stretch mode combination  |
|                              | 5817 cm <sup>-1</sup> (1719 nm) | Asymmetric methylene (C-H) stretch (2v) 1st overtone + aromatic C-H stretch - (2v) 1st overtone |
|                              | 4606 cm <sup>-1</sup> (2171 nm) | C-H bend (3δ) 2nd overtone  |
|                              | 4365 cm <sup>-1</sup> (2291 nm) | C-H stretch + CH <sub>2</sub> deformation combination   |
|                              | 4281 cm <sup>-1</sup> (2336 nm) | C-H stretch + CH <sub>2</sub> deformation combination   |
|                              | 4049 cm <sup>-1</sup> (2470 nm) | C-H stretch + C-C stretch + C-O-C stretch combination   |
| Silicone (dimethyl siloxane) | 6887 cm <sup>-1</sup> (1452 nm) | Si-OH stretch - (2v) 1st overtone   |
|                              | 5721 cm <sup>-1</sup> (1748 nm) | Methyl (C-H) stretch - (2v) 1st overtone  |
|                              | 5173 cm <sup>-1</sup> (1933 nm) | Si-O-H stretch + Si-O-Si deformation combination  |
|                              | 4357 cm <sup>-1</sup> (2295 nm) | C-H bend (3δ) 2nd overtone  |

resins. As mentioned in Chapter 2, the C-H vibrations of a strained ring are particularly well isolated from other absorption bands. In addition, the primary amine functionality in these polymers provides another good NIR functional group.

Many epoxy resin kinetic studies employed the epoxy C-H combination band at 4530 cm<sup>-1</sup> (2208 nm).<sup>13</sup> Others have used the first or second overtones of the C-H stretch at 6060 cm<sup>-1</sup> (1650 nm) or 8620 cm<sup>-1</sup> (1160 nm), respectively.<sup>14</sup> The primary amine functionality has been measured at its first overtone near 6600 cm<sup>-1</sup> (1515 nm) or the combination near 5050 cm<sup>-1</sup> (1980 nm). More specifically, the first overtone region has been reported as a weak asymmetric first overtone NH<sub>2</sub> stretch at about 6850 cm<sup>-1</sup> (1460 nm), an asymmetric/symmetric stretch combination at about 6655 cm<sup>-1</sup> (1500 nm), and an NH<sub>2</sub> symmetric stretch first overtone at about 6550 cm<sup>-1</sup> (1527 nm).<sup>15</sup>

The choice of a good reference point for measuring epoxy resin kinetics was discussed by Lachenal et al.<sup>16</sup> For example, the commonly used 4530 cm<sup>-1</sup> aromatic combination band may have interference from the amine hardener in the formulation. The choice of which epoxy C-H and amine bands to use for the kinetic studies also requires careful examination for potential interferences.

## 12.5 Polymer Properties Determined by NIR

There have been many studies of polymer structure, composition, and properties performed with the aid of NIR

spectroscopy. Some examples include block copolymer composition and crystallinity measurement. Molecular weight has also been determined via end-group analysis. Specific band assignments have been made for many of these studies.

Miller et al.<sup>17</sup> have determined the hard segment and soft segment blocks of poly(ether urethane urea) (PEUU) block copolymers. The hard segments were composed of the reaction product of 4,4'-methylene bis phenylene isocyanate (MDI) with 1,3-propylene diamine, and therefore contained aromatic absorptions and amide functionality. The soft segments were primarily hydroxyl-terminated polytetramethylene oxide. Table 12.3 summarizes the band assignments. These authors also studied the phase separation of these same polymers, with the observations shown in Table 12.4.<sup>18</sup>

**Table 12.3 Band Assignments for PEUU**

| Band Location                             | Description                               |
|---|---|
| <b>Hard Segments</b>                      |   |
| 8541 cm <sup>-1</sup> (1144 nm)           | C-H aromatic 2nd overtone, MDI            |
| 5517 cm <sup>-1</sup> (1690 nm)           | C-H aromatic 1st overtone, MDI            |
| 5669 cm <sup>-1</sup> (1764 nm)           | CH <sub>2</sub> 1st overtone from diamine |
| 6700–6250 cm <sup>-1</sup> (1450–1600 nm) | N-H 1st overtone and C=O 3rd overtone     |
| <b>Soft Segments</b>                      |   |
| 8347 cm <sup>-1</sup> (1198 nm)           | C-H aliphatic 2nd overtone from ether     |
| 5527 cm <sup>-1</sup> (1746 nm)           | C-H aliphatic 1st overtone from ether     |

**Table 12.4** PEUU Phase Separation Bands, from an Annealing Experiment

| Band Location                   | Description                             |
|---------------------------------|---|
| 4912 cm <sup>-1</sup> (2036 nm) | Free urea C=O 2nd overtone              |
| 4868 cm <sup>-1</sup> (2054 nm) | H-bonded urea C=O 2nd overtone          |
| 5214 cm <sup>-1</sup> (1918 nm) | Free urethane carbonyl 2nd overtone     |
| 5051 cm <sup>-1</sup> (1980 nm) | H-bonded urethane carbonyl 2nd overtone |

The conformational changes and molecular interactions of blends of atactic polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene ether (PPE) were studied by Ozaki et al.<sup>19</sup> Table 12.5 and Table 12.6 provide the band assignments they developed from this work.

Conformational structure of polymers, including various crystalline phases, amorphous regions, and anisotropic disordered phases, has also received much attention. Comparisons of mid-IR and NIR using such techniques as 2D synchronous correlations have been applied to a number of polymeric systems. For the common polymer polyethylene, for example, the C-H stretch first overtone and the first combination region have provided information on various crystalline states.<sup>20</sup> A band assignment table that illustrates the shifts that occur with conformation changes is provided as Table 12.7.<sup>21</sup>

Molecular weight can sometimes be measured by NIR spectroscopy, most commonly by end-group analysis. For example, the intramolecularly bonded O-H band near 7140 cm<sup>-1</sup> (1400 nm) has been applied to the estimation of molecular weight of polyethylene glycols.<sup>22</sup> Also, the NH<sub>2</sub> combination band at about 6170 cm<sup>-1</sup> (1620 nm) has been used to determine chain length of amine-ended polysulfone oligomers.<sup>13</sup>

## Acknowledgment

Figures in Chapter 12 are reprinted with permission: Workman, J. Near infrared spectroscopy of polymers and rubbers. In *Encyclopedia of Analytical Chemistry*, Meyers, R. A., Ed., John Wiley & Sons Ltd., Chichester, 2000, 7828–7856.

**Table 12.5** Bands Assignable to PPE in PS/PPE Blends

| Band Location (cm <sup>-1</sup> ) | Description   |
|-----------------------------------|---|
| 8792 (1137 nm)                    | C-H stretch aromatic 2nd overtone                                   |
| 8429 (1186 nm)                    | CH <sub>3</sub> stretch 2nd overtone                                |
| 7338 (1363 nm)                    | 1st overtone of CH <sub>3</sub> str and CH <sub>3</sub> deformation |
| 7236 (1382 nm)                    | 2xC-H str. + C-H in-plane bending, aromatic                         |
| 7149 (1399 nm)                    | 2xC-H str. + C-H in-plane bending, aromatic                         |
| 6770 (1477 nm)                    | 2xC-H str. + C-H in-plane bending, aromatic                         |
| 5970 (1675 nm)                    | C-H stretch aromatic 1st overtone                                   |
| 5869 (1704 nm)                    | CH <sub>3</sub> stretch 1st overtone                                |
| 5752 (1738 nm)                    | CH <sub>3</sub> stretch 1st overtone of blend                       |
| 5679 (1761 nm)                    | CH <sub>3</sub> stretch 1st overtone of blend                       |
| 4967 (2013 nm)                    | C-H str. + 1st overtone of C-H bending, aromatic                    |
| 4647 (2152 nm)                    | C-H stretch aromatic + 1700 cm <sup>-1</sup> sum band of blend      |
| 4443 (2250 nm)                    | C-H stretch + C-H in-plane bending aromatic                         |
| 4414 (2266 nm)                    | Methyl C-H stretch + aromatic C-H bending                           |
| 4312 (2319 nm)                    | Methyl C-H stretch + methyl bending                                 |

**Table 12.6** Bands Assignable to PS in PS/PPE Blends

| Band Location (cm <sup>-1</sup> ) | Description  |
|-----------------------------------|--|
| 8734 (1145 nm)                    | C-H stretch aromatic 2nd overtone  |
| 8225 (1216 nm)                    | CH <sub>2</sub> stretch 2nd overtone   |
| 7192 (1390 nm)                    | 1st overtone of CH <sub>2</sub> str and CH <sub>2</sub> deformation                |
| 7090 (1410 nm)                    | 2X C-H str. + C-H in-plane bending, aromatic                                       |
| 6887 (1452 nm)                    | 2X C-H str. + C-H in-phase out-of-plane wag at 760 cm <sup>-1</sup> aromatic blend |
| 6625 (1509 nm)                    | C-H str 1st overtone + C-H in-plane bend, aromatic                                 |
| 6116 (1635 nm)                    | 2X C-H stretch aromatic  |
| 5519 (1812 nm)                    | C-H str. + 1st overtone of C-H bending, aromatic                                   |
| 5127 (1950 nm)                    | C-H str. + 1st overtone of C-H bending, aromatic                                   |
| 4836 (2068 nm)                    | C-H str. aromatic + sum band at 1800 cm <sup>-1</sup>                              |
| 4574 (2186 nm)                    | C-H str. aromatic + aromatic ring stretch  |
| 4254 (2350 nm)                    | C-H str. + C-H in-plane bend (aromatic)  |

**Table 12.7 Band Assignments for Ethylene Vinyl Acetate Copolymer**

| Band Location (cm <sup>-1</sup> ) | Description  |
|-----------------------------------|--|
| 8850 (1130 nm)                    | C-H str. 2nd overtone (CH <sub>3</sub> , V, A)       |
| 8666 (1154 nm)                    | C-H str. 2nd overtone (CH <sub>3</sub> , V, A)       |
| 8403 (1190 nm)                    | C-H str. 2nd overtone (CH <sub>2</sub> , E, C)       |
| 8210 (1218 nm)                    | C-H str. 2nd overtone (CH <sub>2</sub> , E, A, or D) |
| 7407 (1350 nm)                    | 2X C-H str + C-H def (CH <sub>3</sub> , V, A)        |
| 7278 (1374 nm)                    | 2X C-H str + C-H def (CH <sub>3</sub> , V, A)        |
| 7174 (1394 nm)                    | 2X C-H str + C-H def (CH <sub>2</sub> , E, C)        |
| 7092 (1410 nm)                    | 2X C-H str + C-H def (CH <sub>2</sub> , E, C)        |
| 6954 (1438 nm)                    | 2X C-H str + C-H def (CH <sub>2</sub> , E, C)        |
| 6485 (1542 nm)                    | CH <sub>2</sub> (E, C)*                              |
| 6120 (1634 nm)                    | CH <sub>2</sub> (E, A, or D)*                        |
| 5988 (1670 nm)                    | C-H str. 1st overtone (CH <sub>3</sub> , V, A)       |
| 5945 (1682 nm)                    | C-H str. 1st overtone (CH <sub>3</sub> , V, A)       |
| 5889 (1698 nm)                    | C-H str. 1st overtone (CH <sub>2</sub> , E, A, or D) |
| 5754 (1738 nm)                    | C-H str. 1st overtone (CH <sub>2</sub> , E, A, or D) |
| 5650 (1770 nm)                    | C-H str. 1st overtone (CH <sub>2</sub> , E, A, or D) |
| 5488 (1822 nm)                    | CH <sub>2</sub> (CH <sub>2</sub> , E, A, or D)*      |
| 5429 (1842 nm)                    | CH <sub>2</sub> (CH <sub>2</sub> , E, A, or D)       |
| 5258 (1902 nm)                    | 2X C-O str. + C-H str. (V, A)                        |
| 5192 (1926 nm)                    | CH <sub>2</sub> (E, A, or D)*                        |
| 5128 (1950 nm)                    | C=O str. 2nd overtone (V, A)                         |
| 5076 (1970 nm)                    | CH <sub>2</sub> (E, A, or D)*                        |
| 4955 (2018 nm)                    | CH <sub>2</sub> (E, A, or D)*                        |
| 4878 (2050 nm)                    | CH <sub>2</sub> (E, A, or D)*                        |
| 4757 (2102 nm)                    | C-H str. + C=O str. (V, A)                           |
| 4677 (2138 nm)                    | C-H str. + C=O str. (V, A)                           |
| 4591 (2178 nm)                    | C-H str. + C=O str. (V, A)                           |

*Note:* E and V refer to ethylene and vinyl acetate units, respectively. C, A, and D denote the orthorhombic crystalline phase, amorphous phase, and anisotropic disordered phase, respectively.

\* Due to complex combination modes of CH stretching, CH<sub>2</sub> wagging, twisting, or rocking vibrations.

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# Chapter 13

## **History of Near-Infrared Applications**

### 13.1 History of NIR for Industrial Chemicals

The application of near-infrared (NIR) spectroscopy to the study of basic chemicals began in the 1800s. Following Herschel's discovery of the phenomenon of radiation beyond the visible region,<sup>1</sup> Abney and Festing recorded spectra of organic compounds photographically in 1881 and noted that they were related to the presence of hydrogen atoms.<sup>2</sup> In 1896, Donath<sup>3</sup> measured some organic compounds. In 1899–1900, Luigi Puccianti at the University of Pisa used a single quartz prism to study 15 hydrocarbon compounds.<sup>4</sup> In 1904–1905, William W. Coblentz, working at the Carnegie Institute in Washington, DC,<sup>5,6</sup> measured the spectra of a number of compounds including benzene and chloroform from 800 to 2800 nm using a quartz prism and radiometer measured with the aid of a telescope.<sup>7</sup> In 1922, Joseph W. Ellis at the University of California developed a recording spectrograph, measured a large number of organic compounds, and made many fundamental band assignments.<sup>8</sup> Other early work on specific chemicals included that done at the U.S. Department of Agriculture (USDA) by Liddel and Wulf,<sup>9</sup> and at the US Bureau of Standards by Rose,<sup>10</sup> both in the 1930s.

In the 1940s, advances in instrumentation and the availability of commercial NIR instruments helped to bring about applications in the chemical and polymer industries. In 1949, Hibbard and Cleaves at the Lewis Flight Propulsion Laboratory in Cleveland, Ohio, studied hydrocarbon absorptions with the goal of analyzing octane and cetane numbers in reciprocating engine fuels, analyzing lubricating oils, and determining structure of polymers.<sup>11</sup> In the late 1940s and early 1950s, Lauer and Rosenbaum of Sun Oil also worked with hydrocarbons in the second overtone region.<sup>12</sup> Lauer and Rosenbaum mention studying natural and synthetic plastics including oriented nylon, polyvinyl chloride, and other polymers.

At about 1951, both Wilbur Kaye at Tennessee Eastman and Harry Willis in the Plastics Division of ICI in the United Kingdom began exploring NIR. Kaye modified a Beckman DU UV instrument and worked on the development of the Beckman DK for the NIR. Kaye thoroughly discussed the spectra of several compounds, including bromoform, chloroform, methylene chloride, benzene, methanol, and *m*-toluidine.<sup>13</sup> He cited potential application of the spectral region to the analysis of mixtures of

organic compounds, including water in hydrocarbons and other solvents, alcohols in hydrocarbons, acids, amines, benzene, and olefins in hydrocarbons.

Harry Willis initially designed and built an instrument with a small CsI prism.<sup>14</sup> He worked with copolymer analyses, using thicker sheets of polymer than was possible with mid-IR. Measurements were made quickly and directly.<sup>15</sup> He was able to estimate monomer content, determine molecular weight by end-group analysis, and measure copolymers such as butadiene/styrene.

Two other industrial chemists who worked with developing NIR applications in the 1950s were Robert Goddu of Hercules Powder Company (now Hercules Incorporated) and Kermit Whetsel of Tennessee Eastman. Goddu explored a number of different applications including the measurement of epoxide functionality and unsaturation in polymers and phenolics. His review chapter published in 1960 included many of these applications.<sup>16</sup> Whetsel also studied a number of applications including phenols, fuels, and polymers, and included those in a review article published in 1968.<sup>17</sup>

Following these and other industrial applications of NIR in the 1950s–1960s, the field became somewhat stagnant for laboratory analyses with the advent of nuclear magnetic resonance (NMR) and other newer technologies that had greater distinguishing capabilities. Online process instruments, especially for water or moisture measurements, were an exception. These came into use in the 1940s and continue through today, but they were primarily filter instruments measuring only a few specific wavelengths.

With the rise of NIR reflection instrumentation and chemometric data treatments for rapid, direct control measurements, the interest in NIR for industrial applications became greater again. Process control applications, either rapid laboratory measurements or real-time online analyses, benefited the most from the new technologies. Older applications, such as hydroxyl number, polymer properties, water measurement, and fuel analyses have been revisited.

### 13.2 History of NIR for Food and Agriculture

It is generally recognized that the history of the application of near IR to the food and agricultural industry began with Karl Norris at the USDA. In fact, Norris's work was



instrumental in the major renaissance of the NIR spectral region, especially with regard to its application to direct, solids-sampling measurements.

As Norris related in a recent review article,<sup>18</sup> the first work was done beginning in 1949 using visible to low-wavelength NIR radiation to grade eggs. An unpublished spectrum taken in 1952 showed a water overtone at about 750 nm, but the peak was not found to be useful in predicting egg quality, and he did not pursue NIR for about 10 years in favor of visible spectrometry for color sorting.

In 1962, Norris, Hart, and Golumbic first published an NIR application, the determination of moisture in methanol extracts of seeds.<sup>19</sup> This was followed by transmission measurements of moisture in intact seeds with carbon tetrachloride used for reducing scattering losses.<sup>20</sup> It was the leap to diffuse reflection, however, that propelled NIR spectroscopy to wide application in agriculture and, eventually, many other industries as well. This shift required instrument modifications and the segment/gap derivative multiple linear regression approach to calibration that was pioneered in Norris's laboratory.

During the first stage in the development of NIR for food and agriculture, moisture analysis and nutrient determinations were driving forces. These measurements were important because the economic value of the products such as wheat is based on the dry weight and the protein content. Wet chemical methods for these analyses were costly and time consuming, and not available at the points of sale. Early examples include the measurement of moisture in grain<sup>21</sup> and soybeans.<sup>22</sup>

In Canada, Phil Williams<sup>23</sup> of the Canadian Grain Commission purchased one of the first commercial instruments available and proceeded to initiate programs throughout his country to improve the measurement of moisture and protein in wheat. Similar efforts were launched in other large grain-producing countries such as Australia and Russia.

Applications in other agricultural products, such as corn<sup>24</sup> and tobacco,<sup>25</sup> followed. Forage analysis was another big driver of networked analyzer systems.<sup>26</sup> The technology then rapidly spread to processed foods such as chocolate, baked goods, meat and dairy products, and snack foods. In Japan, the bulk of the NIR applications are in food and agriculture.<sup>27</sup>

The agricultural products were primarily dependent upon a small number of "protein," fat, moisture, and

carbohydrate wavelengths that were determined empirically through wavelength selection of large sample sets. In addition, the food and agricultural industries developed some nonchemical measurements, such as hardness of wheat, which was dependent upon particle size.<sup>28</sup> There were some limited efforts to perform spectral band assignments, but most of the calibrations were empirical. The complexity of natural products discourages very specific band assignments. For example, the measurement of "protein" involves grouping many types of protein molecules. Early wavelengths used to measure protein, oil, and water were the combination bands at 2180 nm for protein, 2305 nm for oil, and 1940 nm for water.<sup>29</sup> Tabulations of some general band assignments for foods and agricultural products can be found in the books by Osborne and Fearn,<sup>50</sup> and Williams and Norris books.<sup>51</sup>

### 13.3 History of NIR for Pharmaceuticals

NIR spectroscopy was used by pharmaceutical research groups at least since the late 1960s, initially to study hydrogen bonding of amines and amides or to perform quantitative analyses of these functional groups in solution. Examples include studies by S. Edward Krikorian at the University of Maryland,<sup>30–33</sup> Yumiko Tanaka and Katsunosuke Machida of Kyoto University,<sup>34,35</sup> and L. A. Strait and M. K. Hrenoff of the University of California,<sup>36</sup> all from pharmacy departments. In 1966, Sinsheimer and Keuhnelian<sup>37</sup> analyzed pharmaceutically active amine salts in pressed pellets. In 1967, Oi and Inaba determined phenacetin in preparations by NIR.<sup>38</sup> In a 1977 article, Zappala and Post reported using solution NIR to measure meprobamate in tablets, capsules, suspensions, and injectables.<sup>39</sup> This was an advantage over previous mid-IR methodology because, in the NIR, the amine combination band at 1958 nm is separated from interference by hydroxyls and thus did not need to be chromatographically separated from an alcohol stabilizer.

The use of "modern" NIR in the pharmaceutical industry began soon after its use in the food and agricultural industries. Early applications included the measurement of moisture, particle size, the determination of composition, and identification of raw materials.

NIR moisture analyzers existed in industry long before the modern mode of multivariate NIR analysis, and the earliest applications of NIR in the pharmaceutical industry also

began with moisture determinations. As examples, Beyer et al.<sup>40</sup> measured water in excipients directly, and Sinsheimer and Poswalk looked at water by extracting into acetone.<sup>41</sup>

Particle size was also a subject of early experiments. Although NIR spectroscopy alone cannot provide a particle size distribution the way other technologies such as image analysis, screening, and light scattering do, it is possible to estimate an average particle size by manipulating the underlying scattering curve. When coupled with low-angle light scattering, NIR has been shown to be quite accurate.<sup>42</sup>

Quantitative analysis of tablets and other dosage forms were also performed early in the current wave of NIR. In 1982, Rose et al. reported the direct analysis of meglumine and meglumine diatrizoate in injectable solutions, for example.<sup>43</sup> In 1986, Whitfield<sup>44</sup> developed a method to measure the amount of lincomycin in granulations for veterinary purposes. This was the first NIR method accepted by the Food and Drug Administration as a primary method.<sup>45</sup>

Whitfield's article also represents an example of the use of discriminant analysis in pharmaceutical methods. Probably the first work in this field was done by Rose in 1982<sup>46</sup> when he showed that a number of structurally similar drugs could be identified. This was followed by the application of Mahalanobis distances to pharmaceutical raw materials.<sup>47</sup> A review of the uses of NIR in pharmaceuticals was done by Ciurczak in 1987<sup>48</sup> and a chapter written in 1992 and revised in 2001.<sup>49</sup> The field continues to expand.

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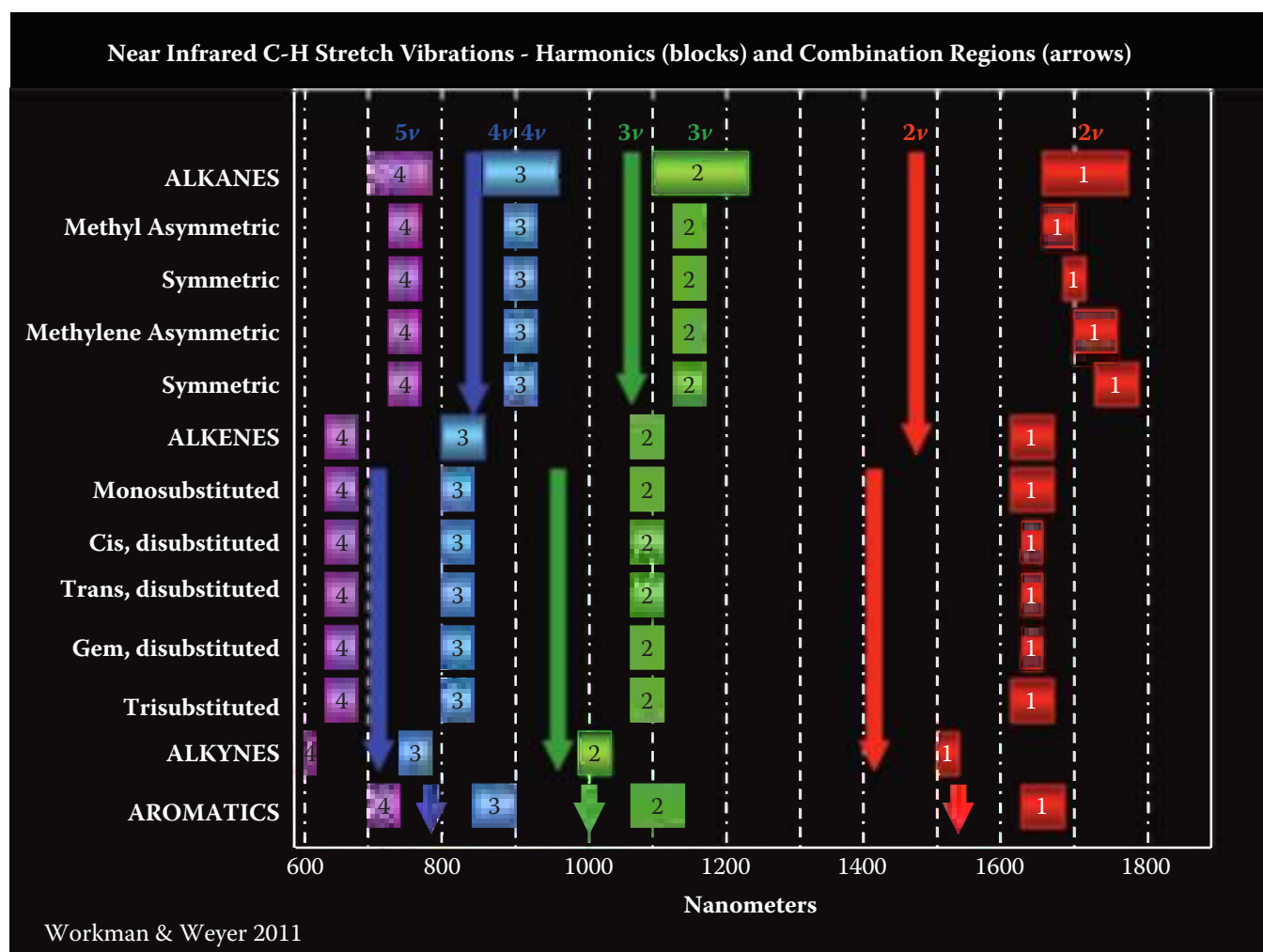


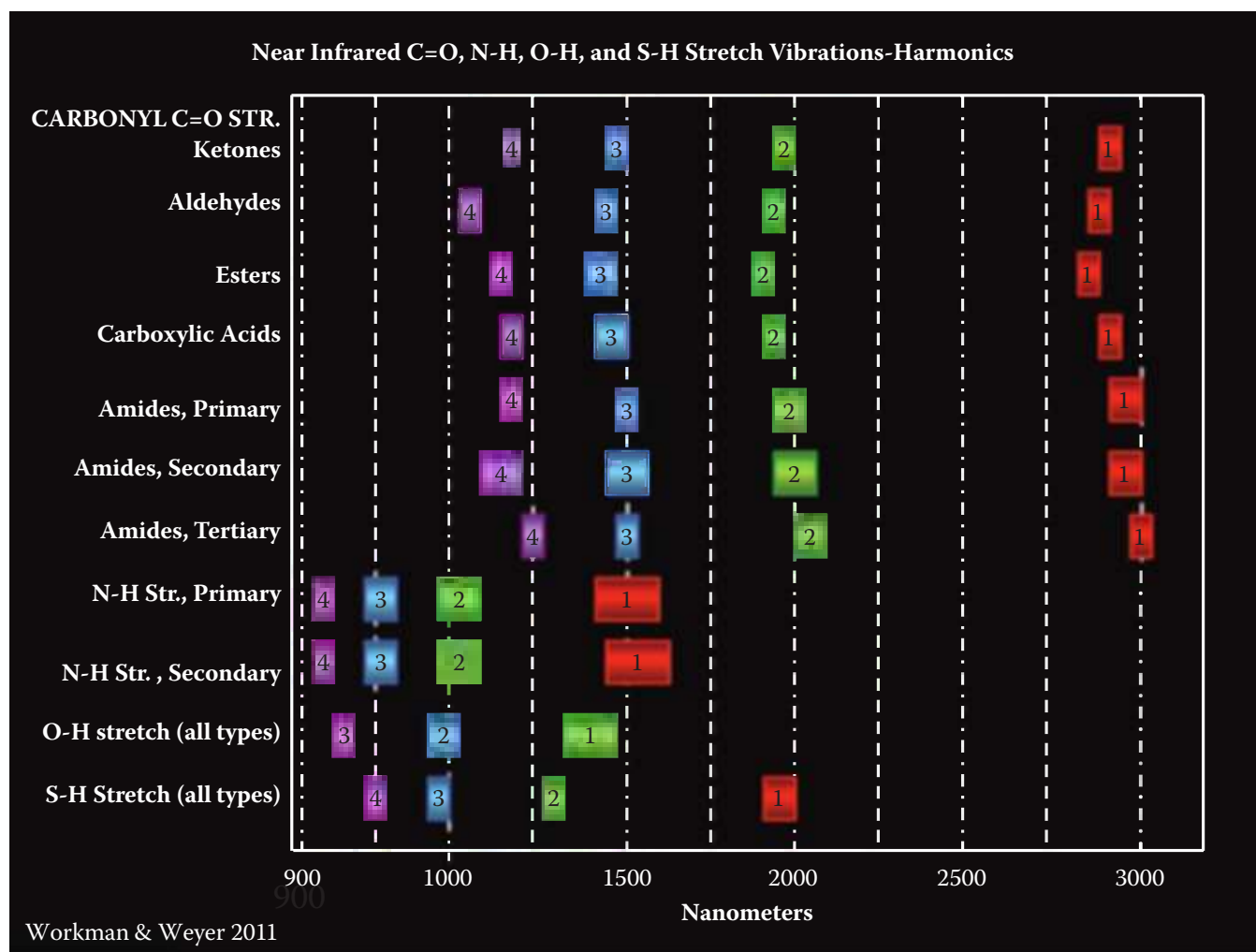
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# Appendix A

## NIR Absorption Band Charts Overview







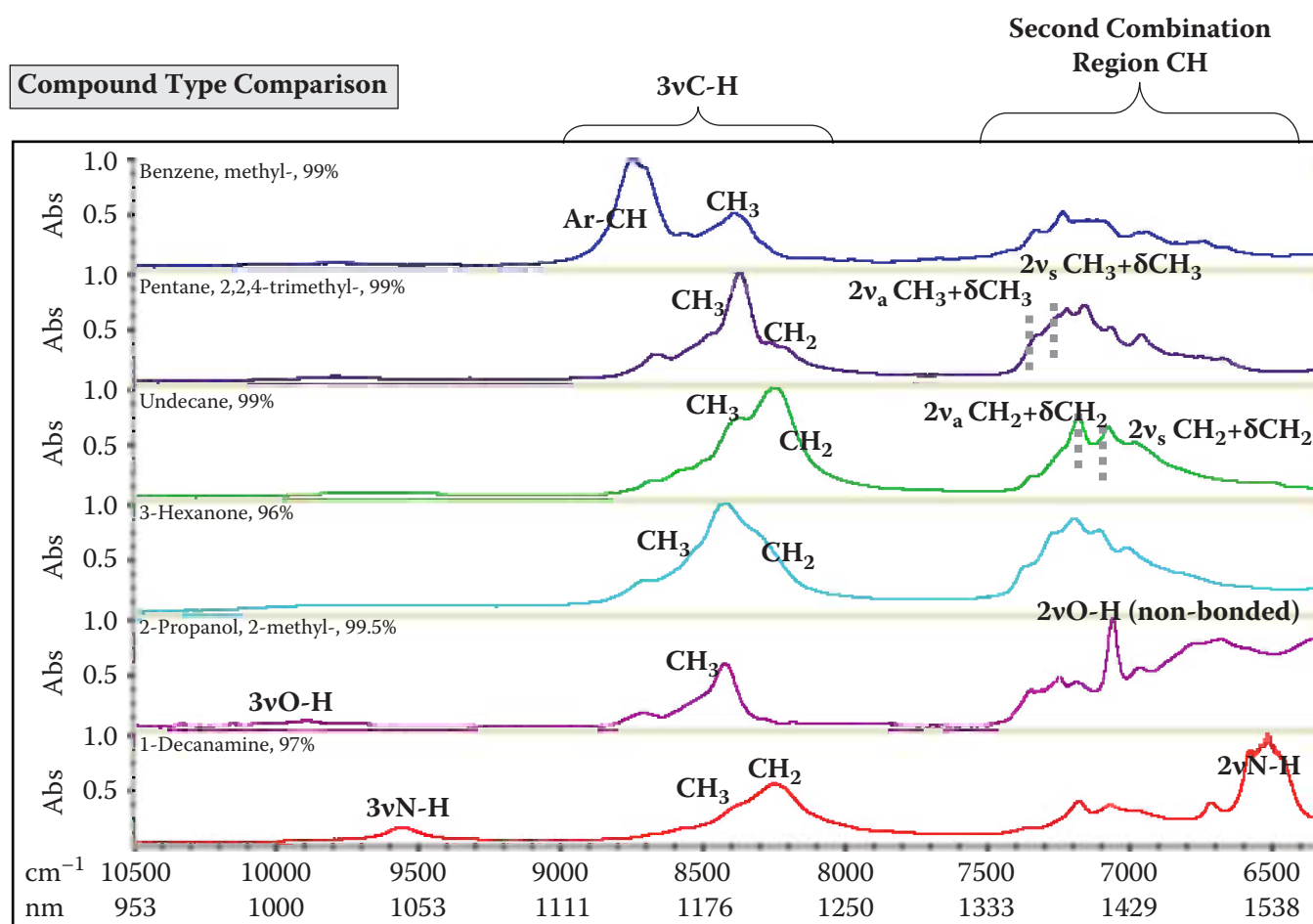
# Appendix B

## Spectra–Structure Correlations\*

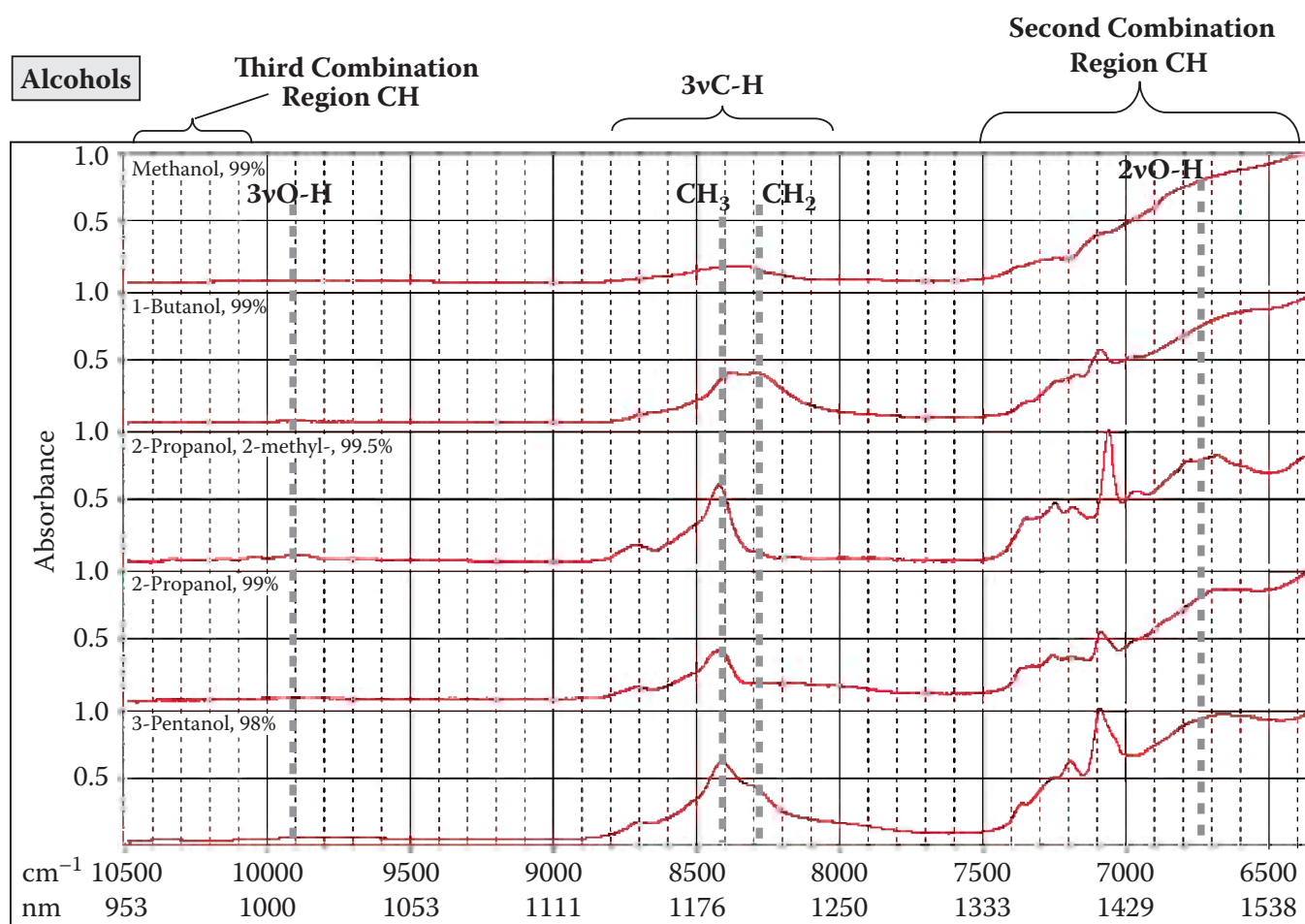
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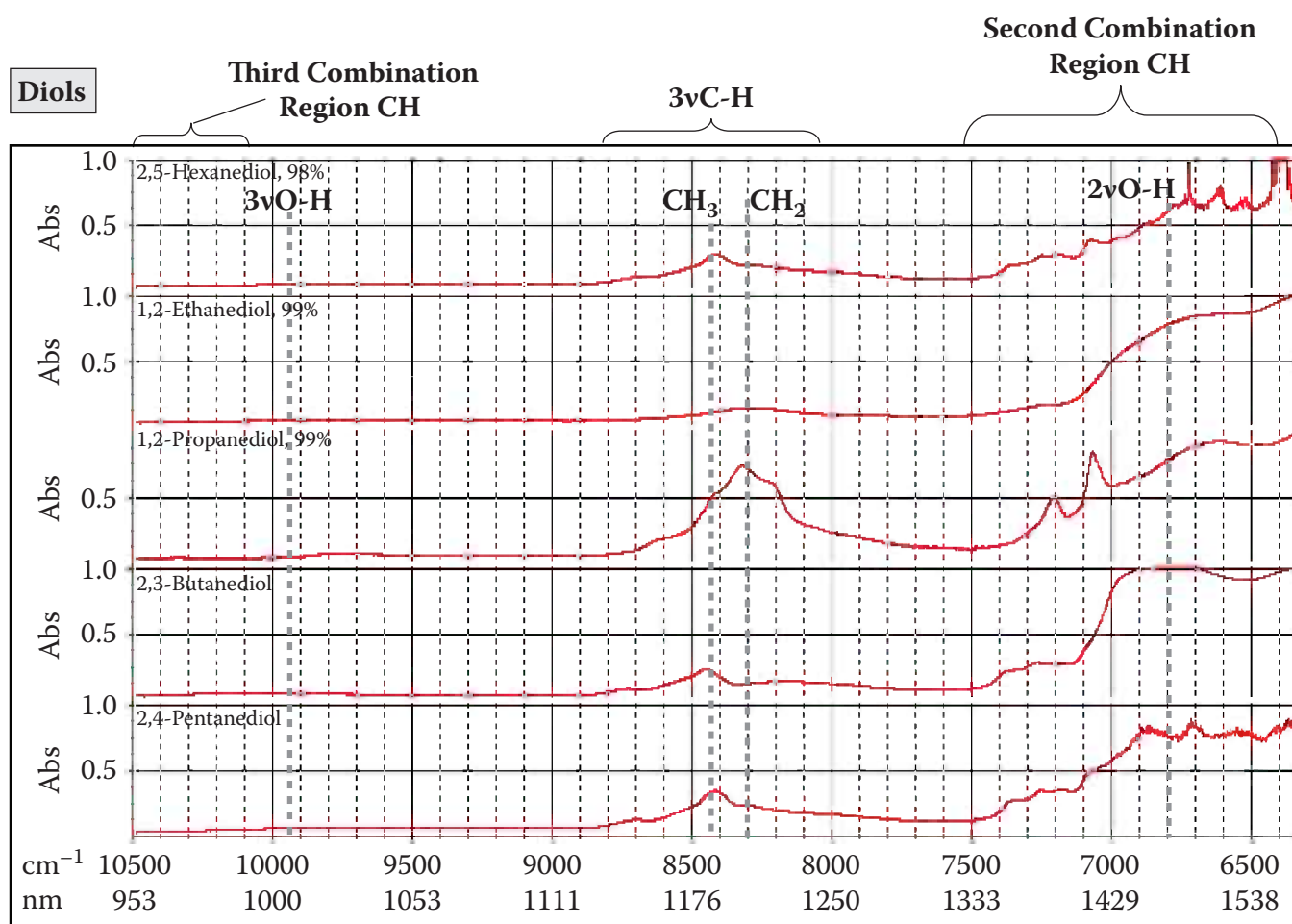
\* Spectra used by permission “NIR Spectra of Organic Compounds,” © Wiley-VCH, ISBN 3-527-31630-2.

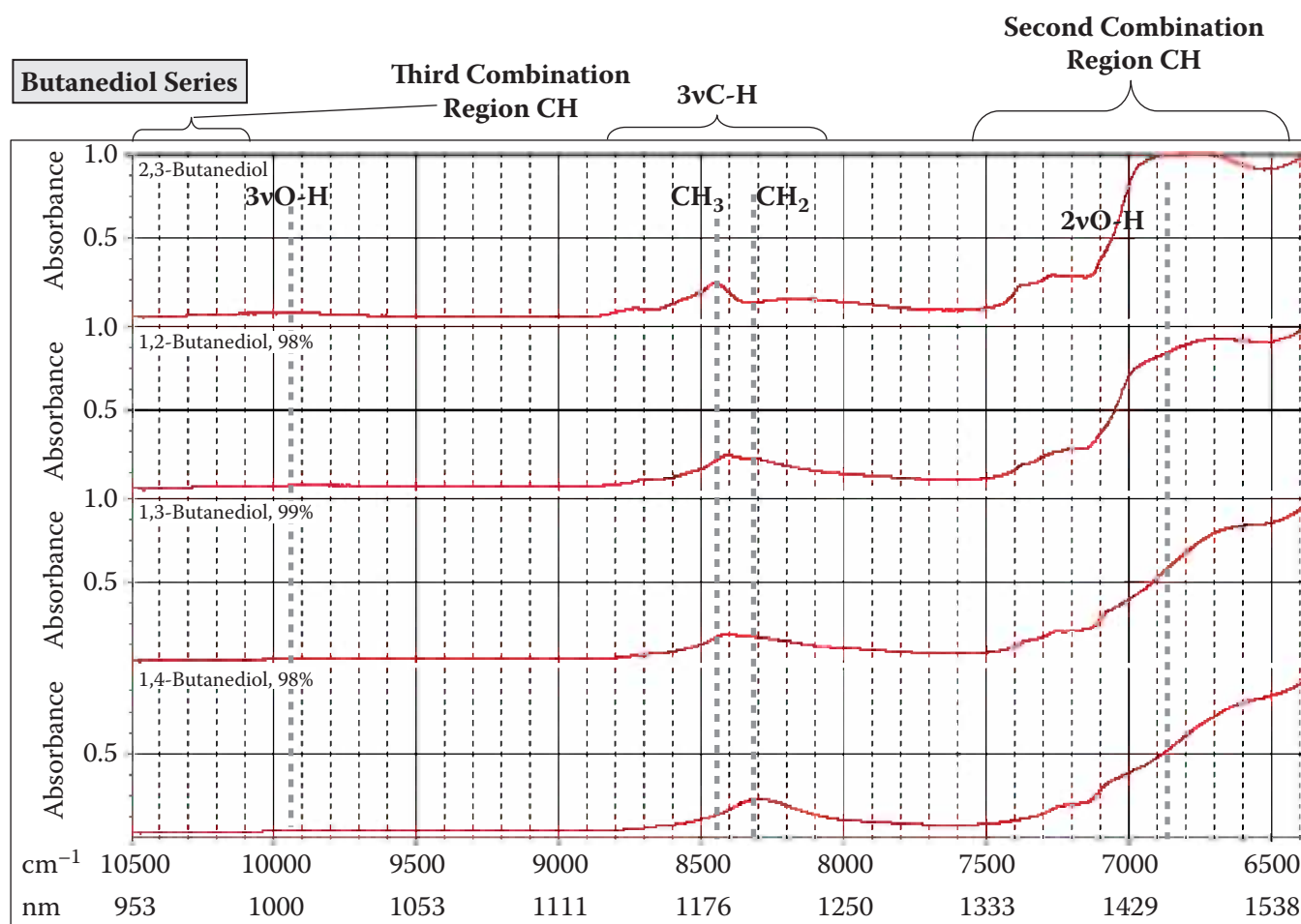
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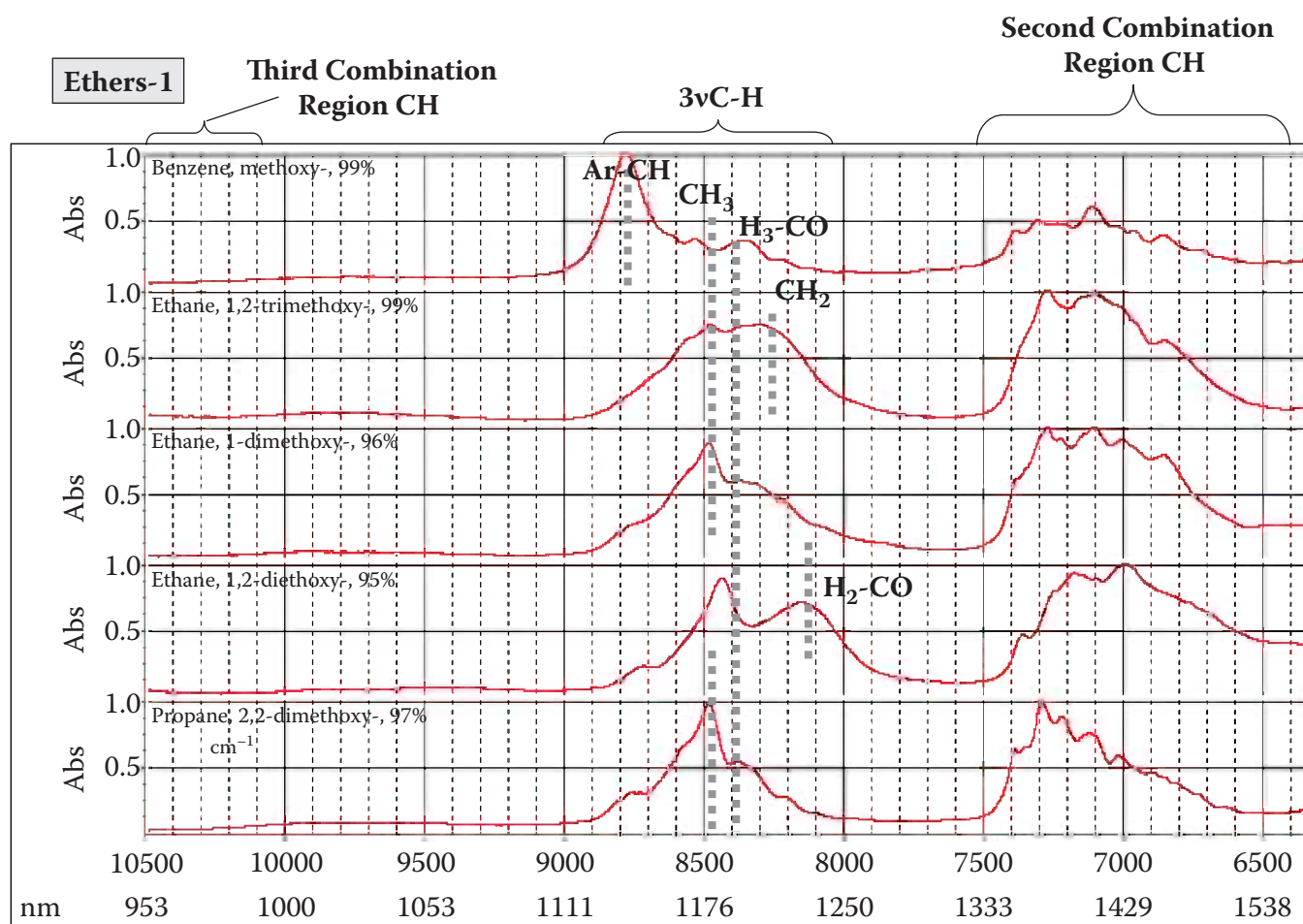


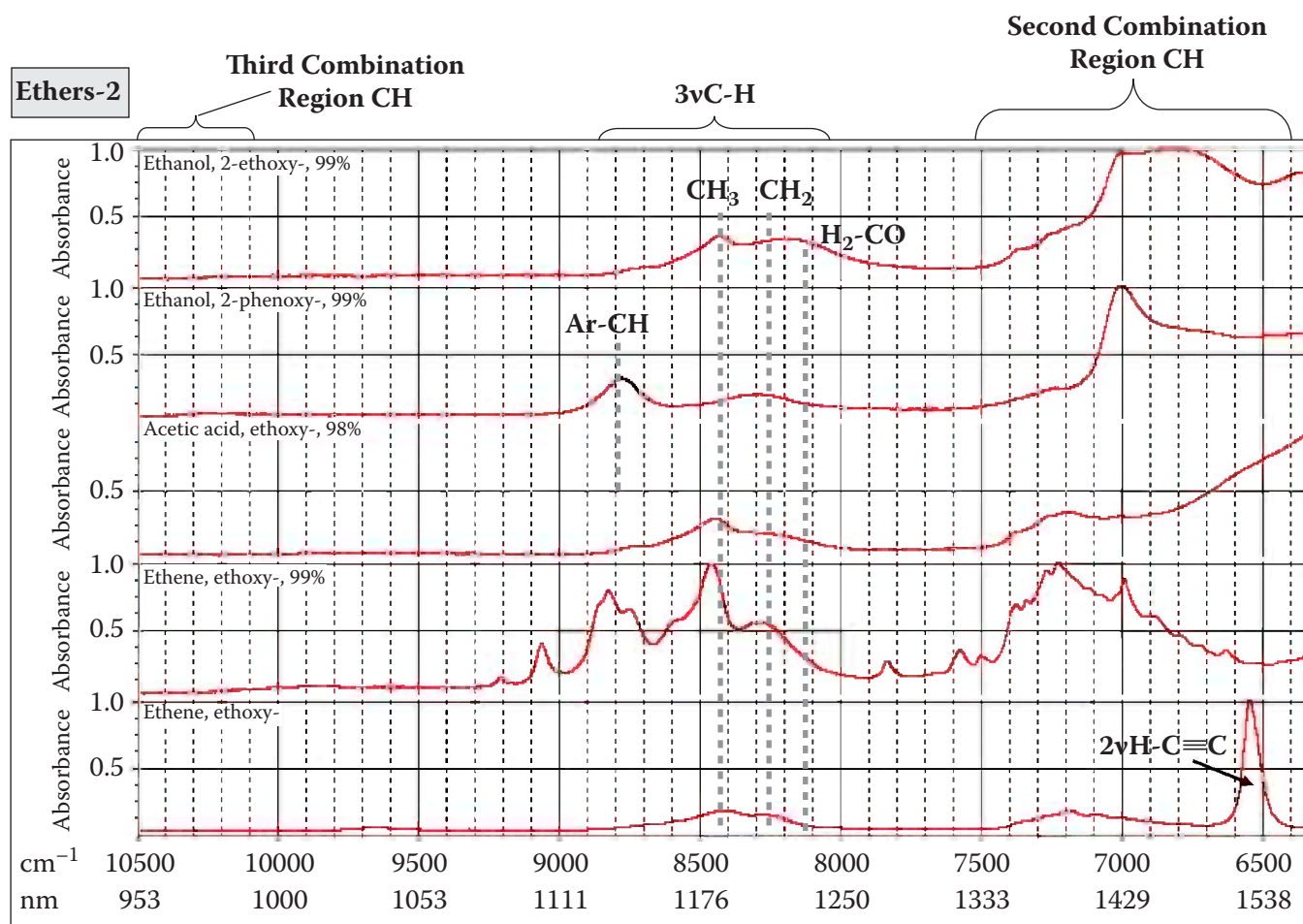


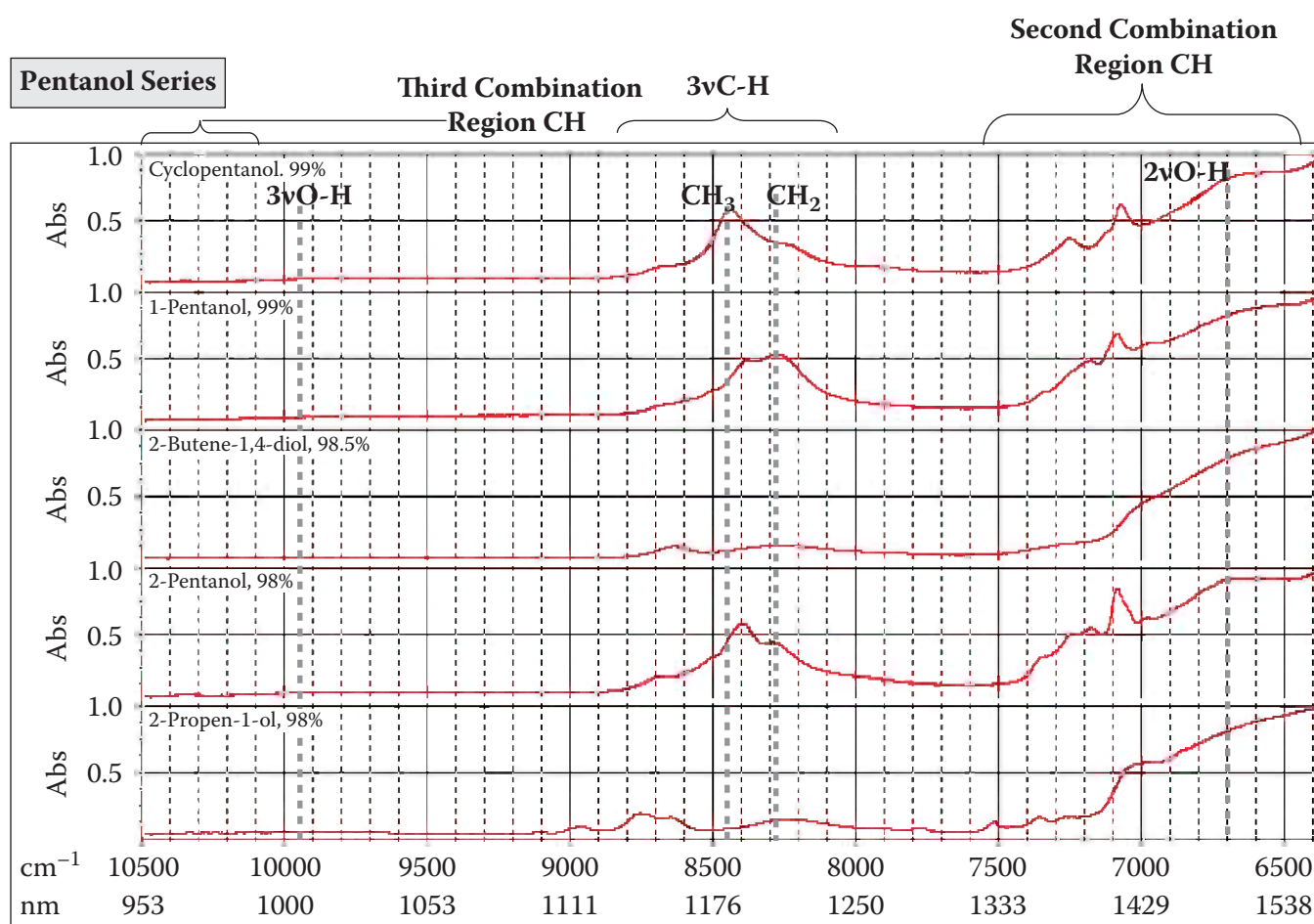


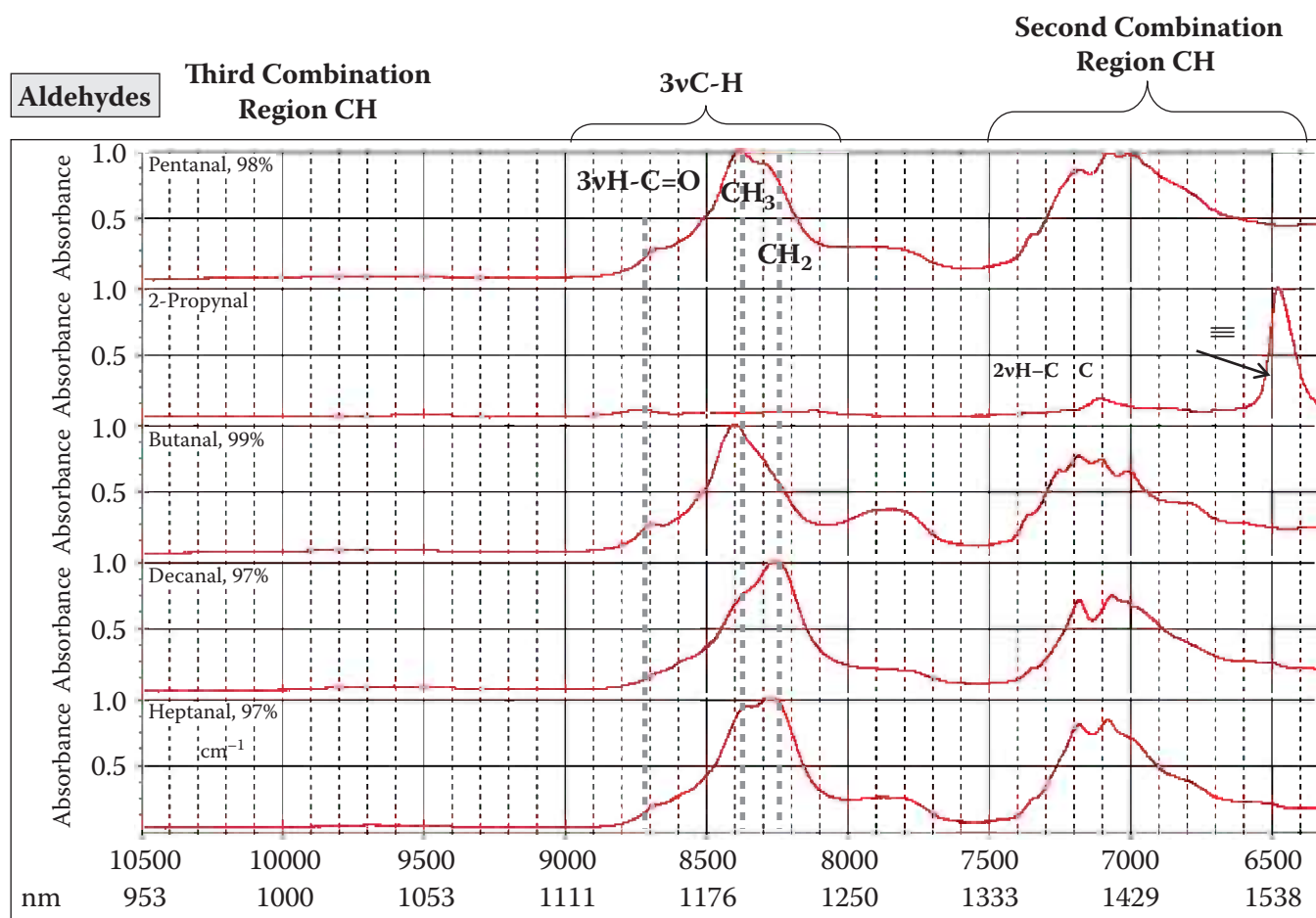


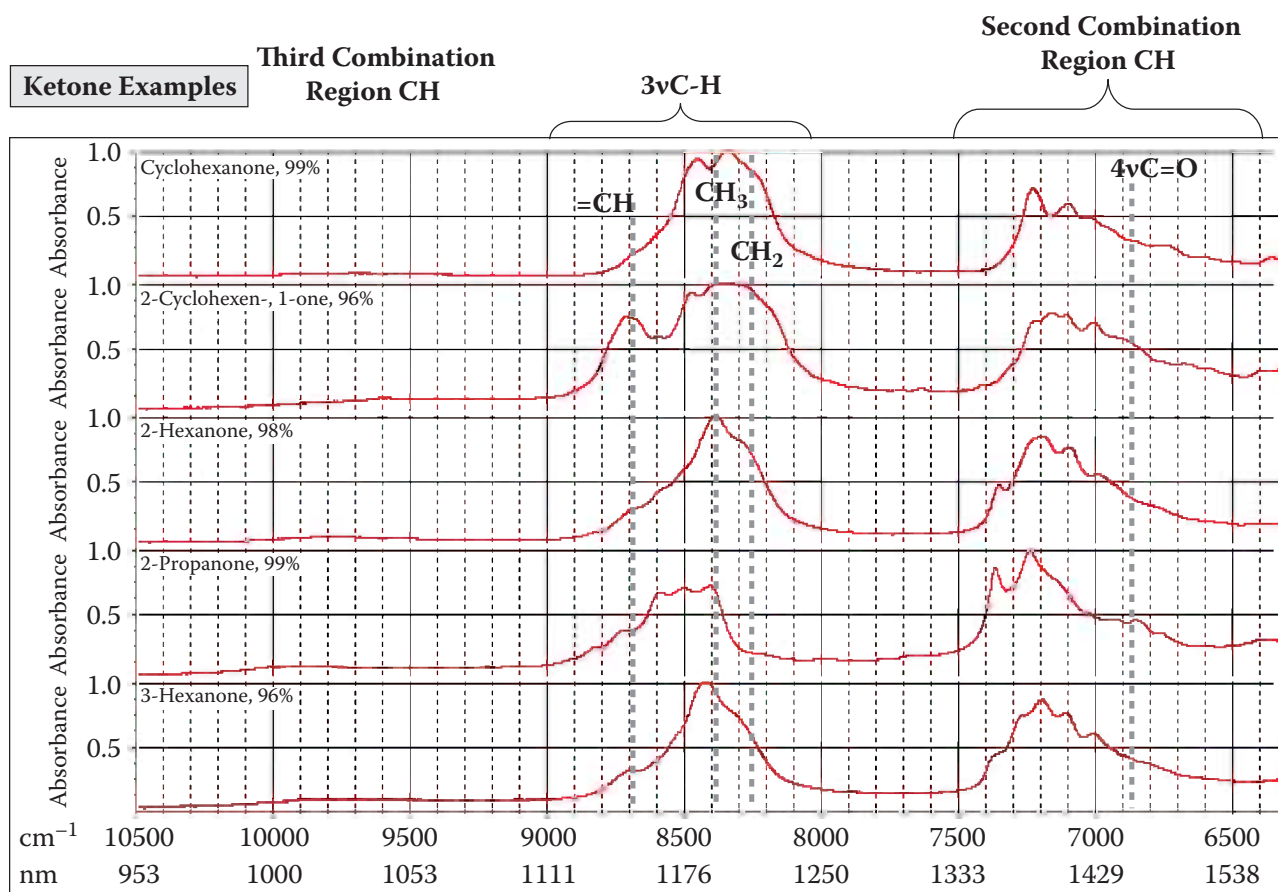




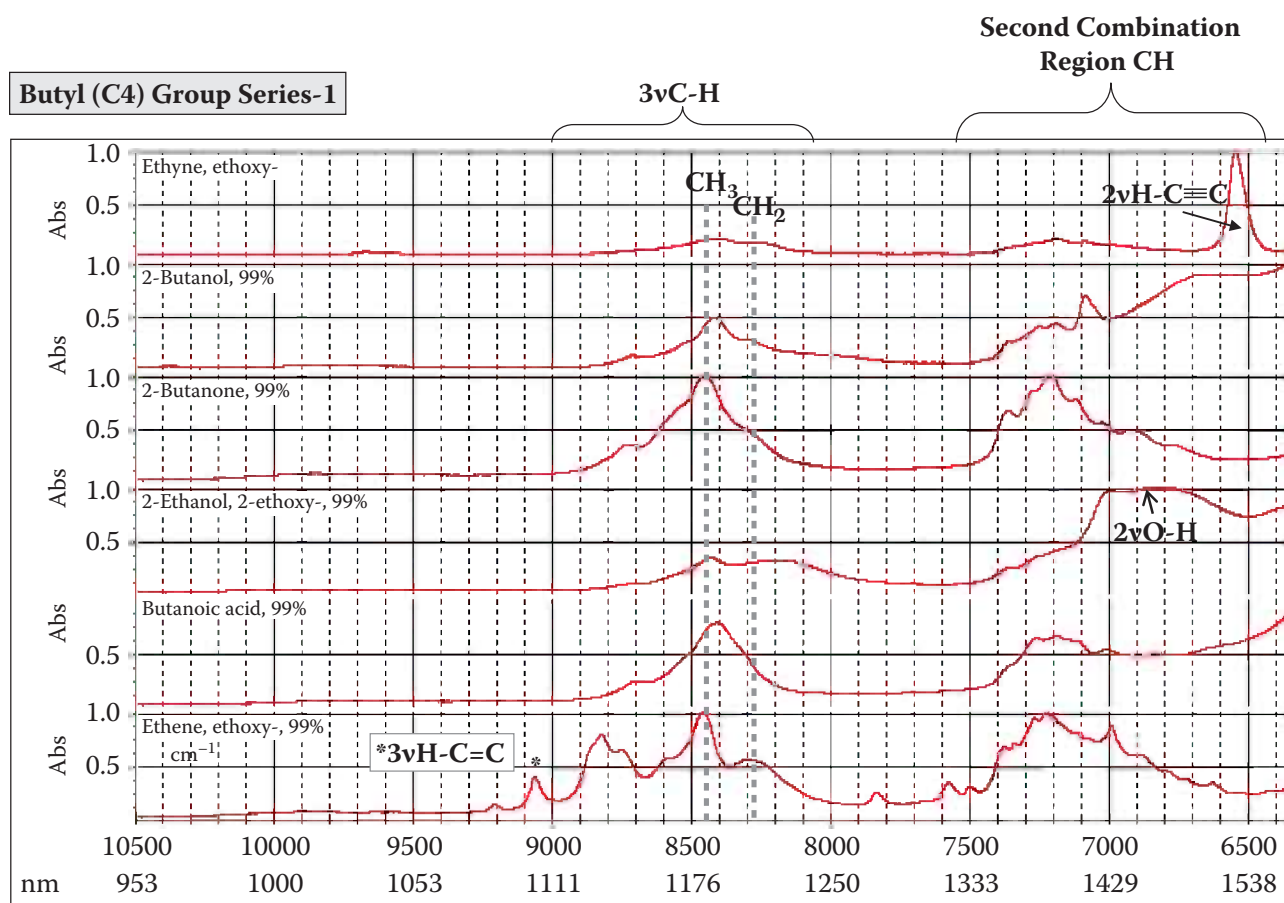


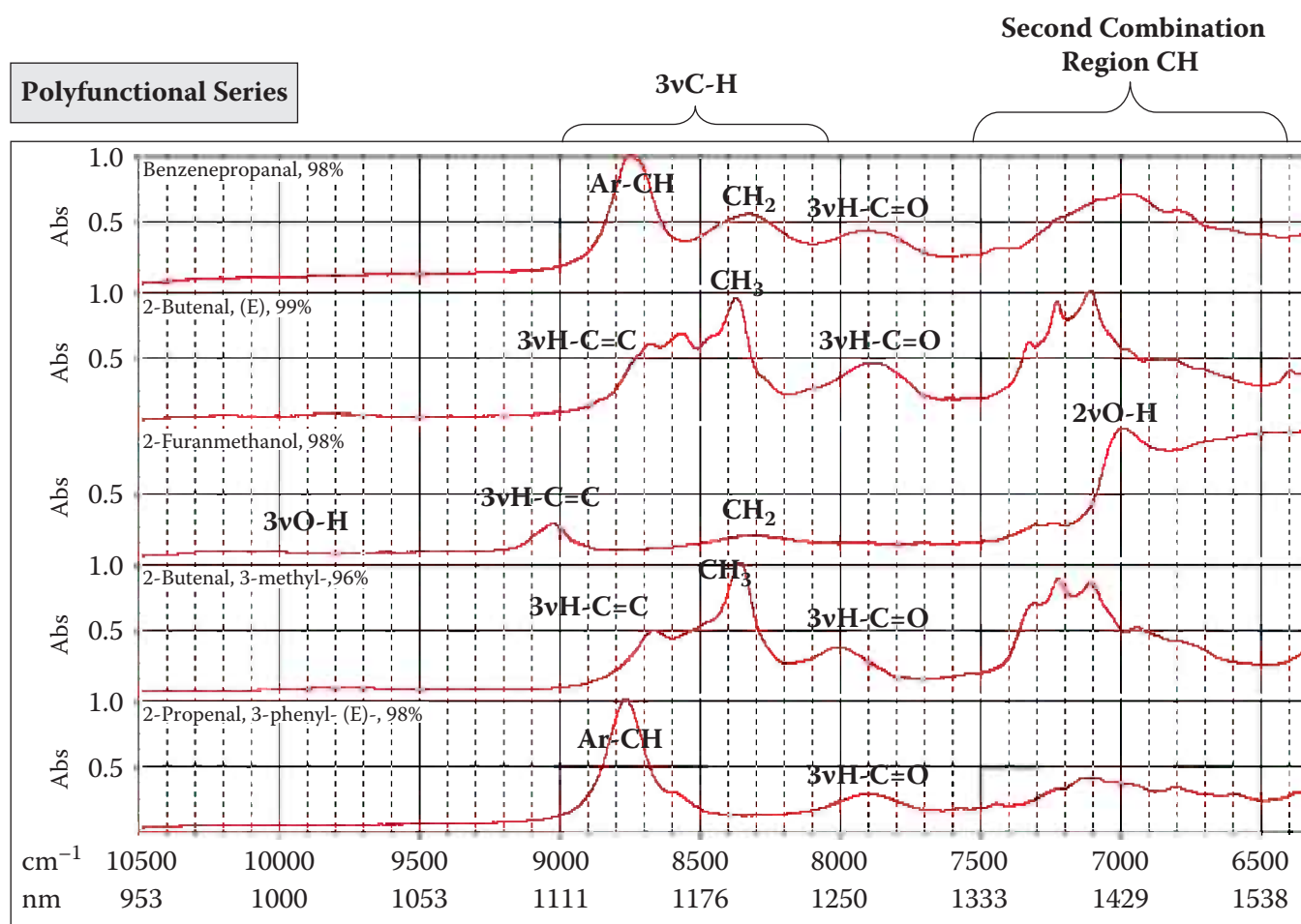


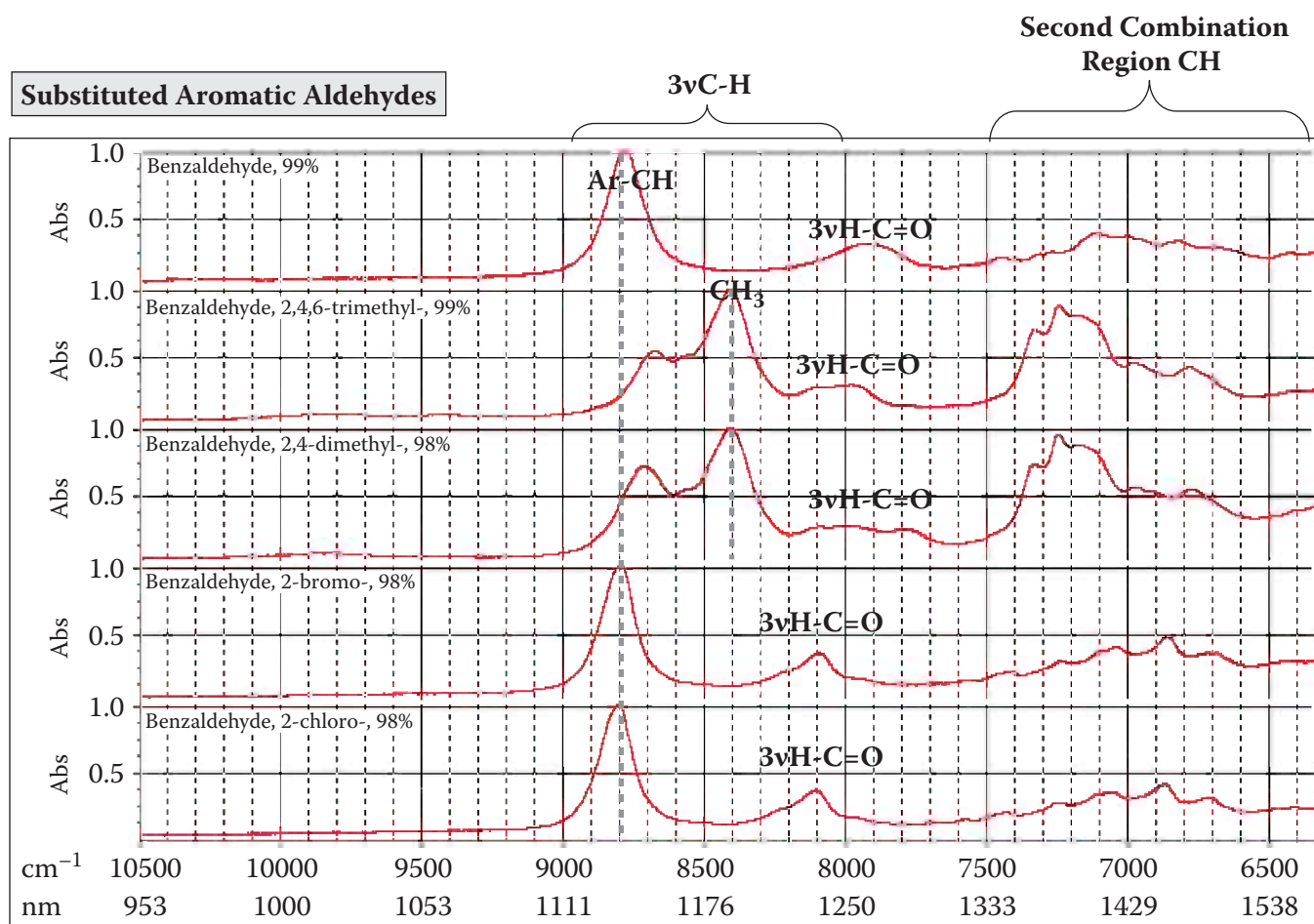


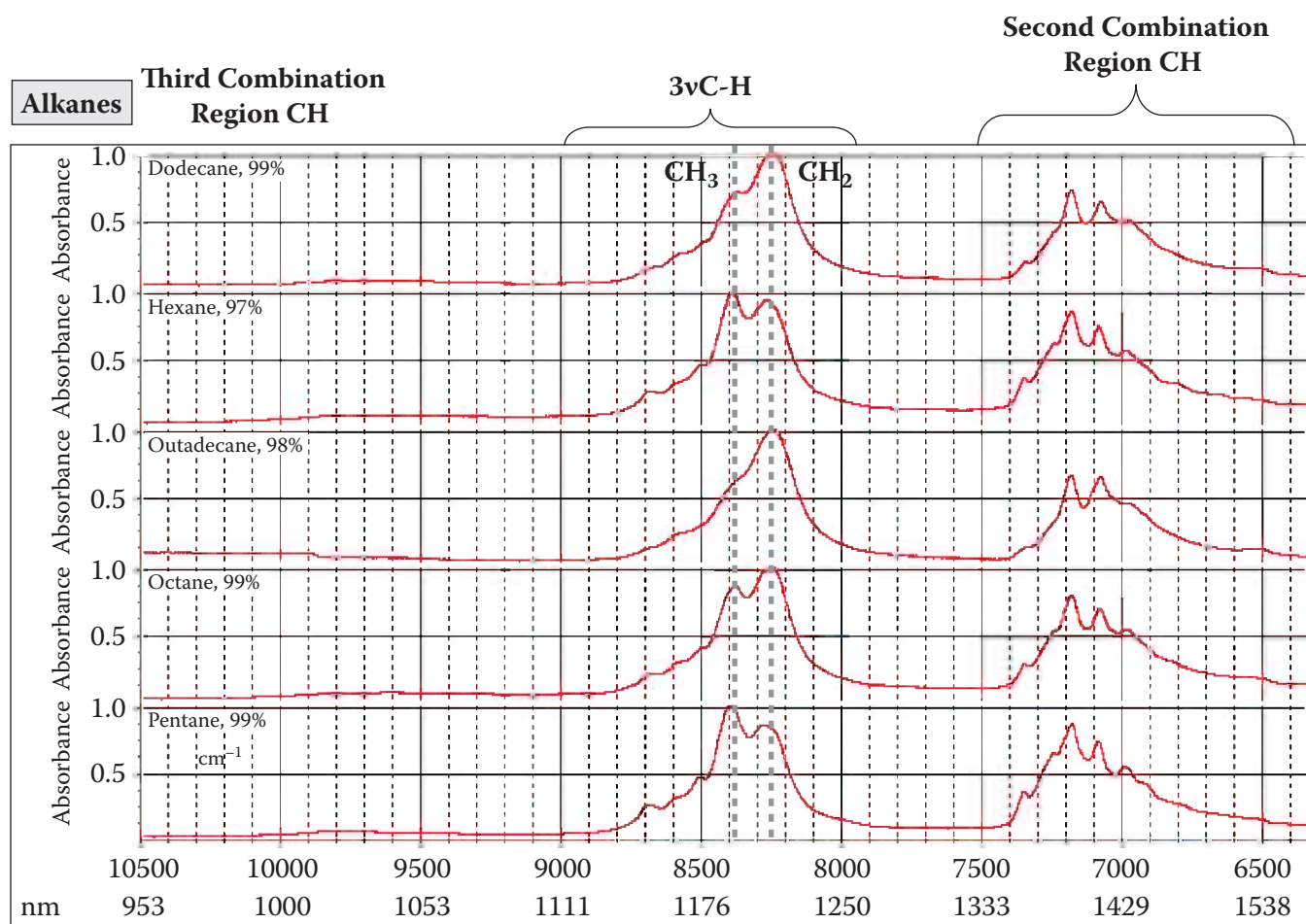


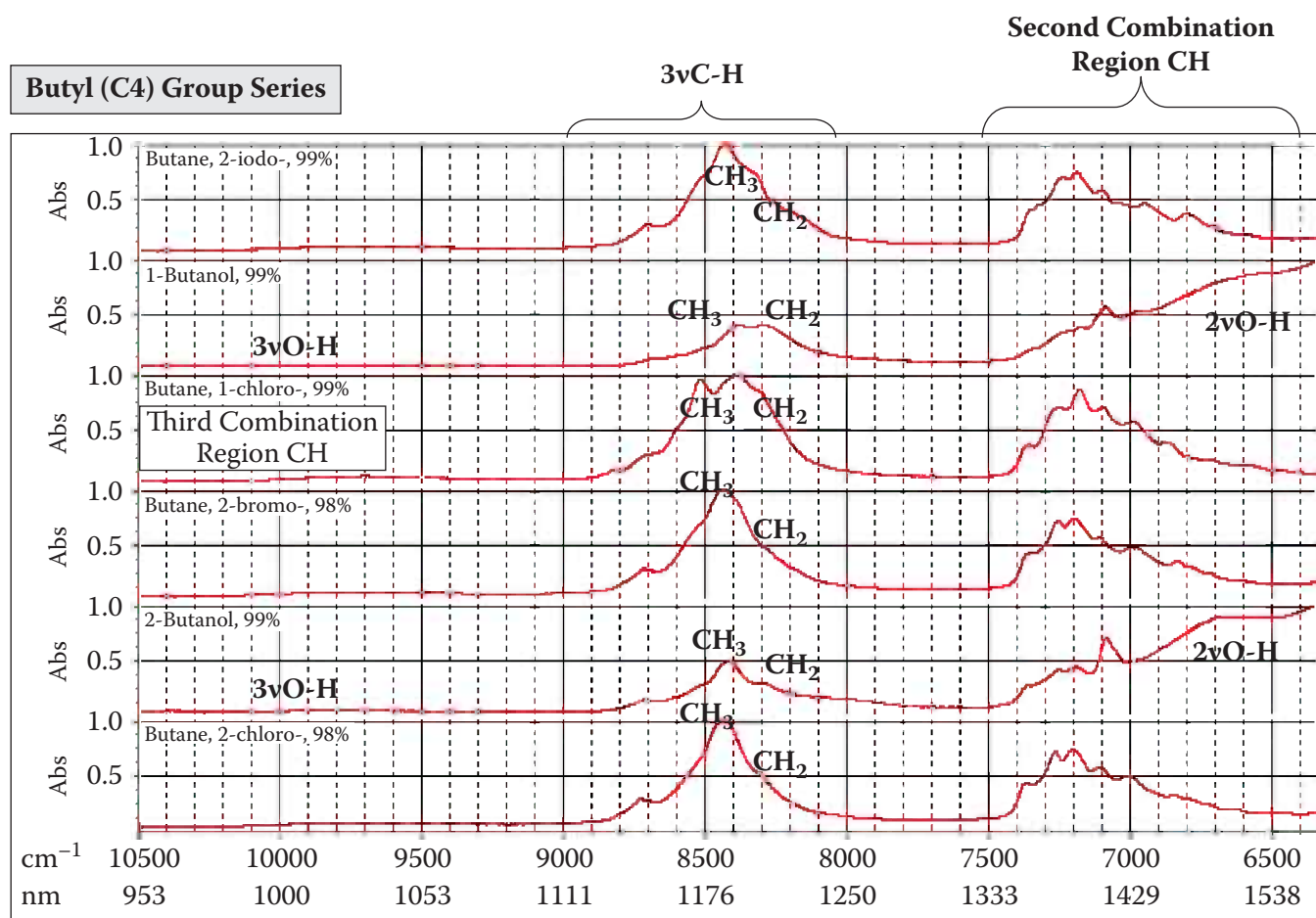


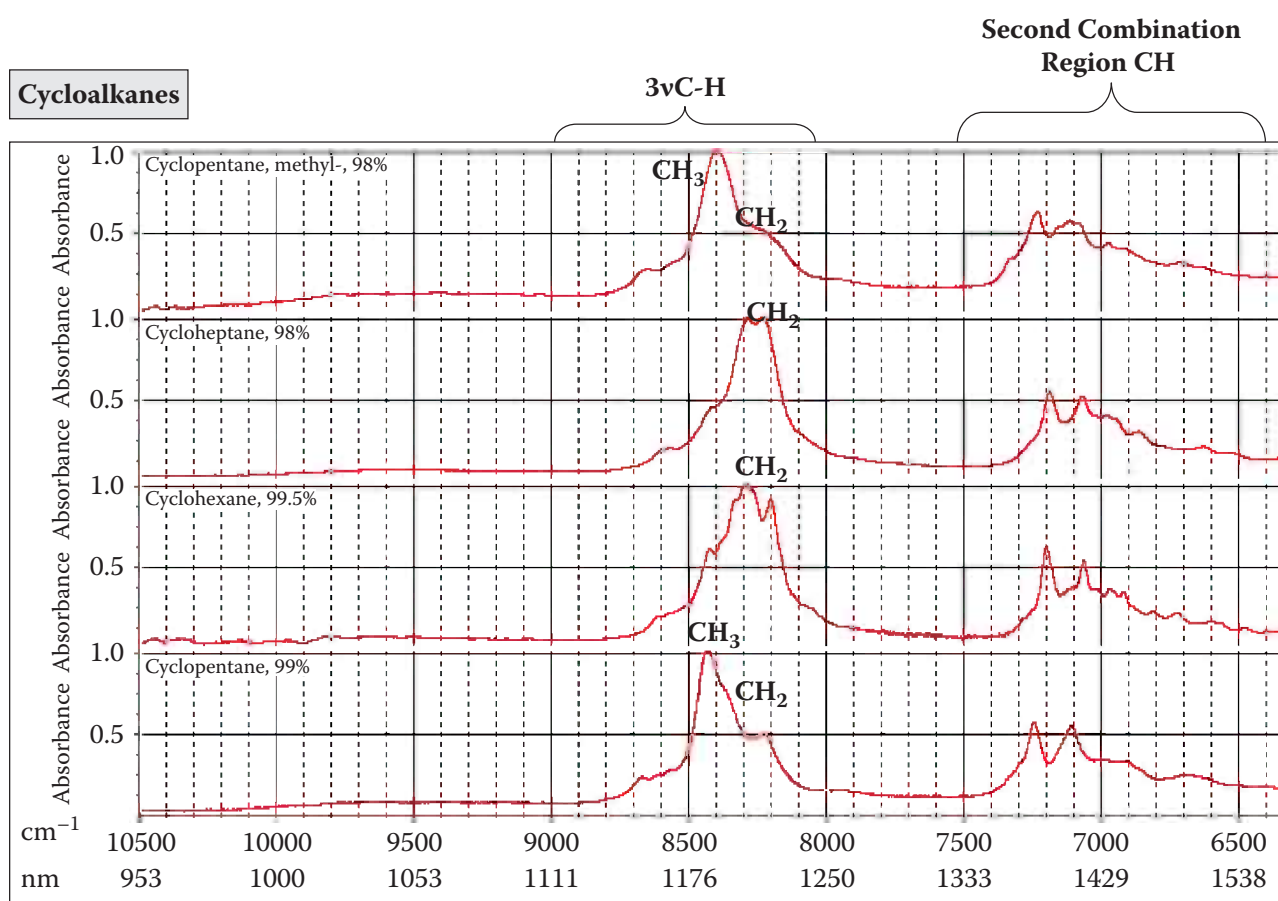


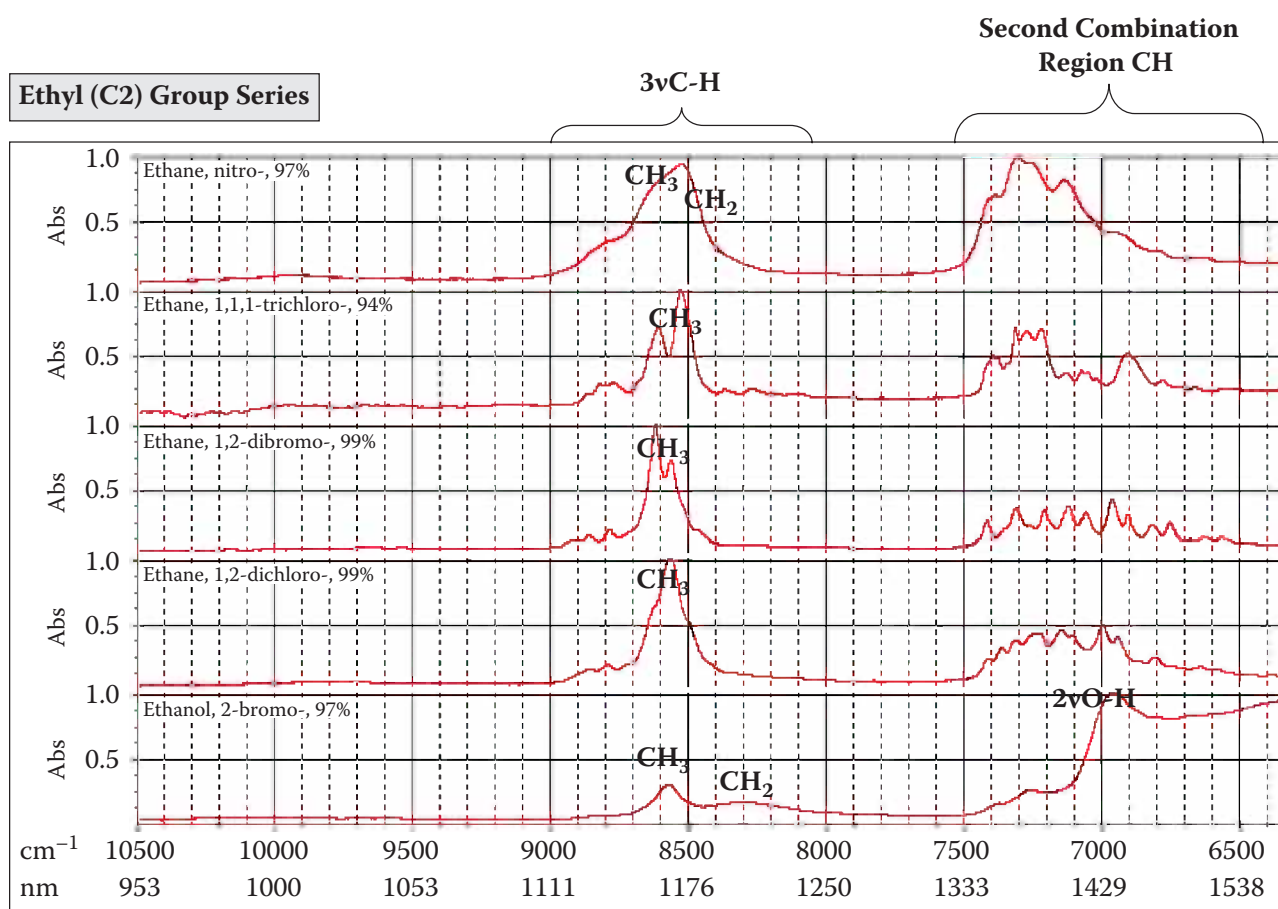


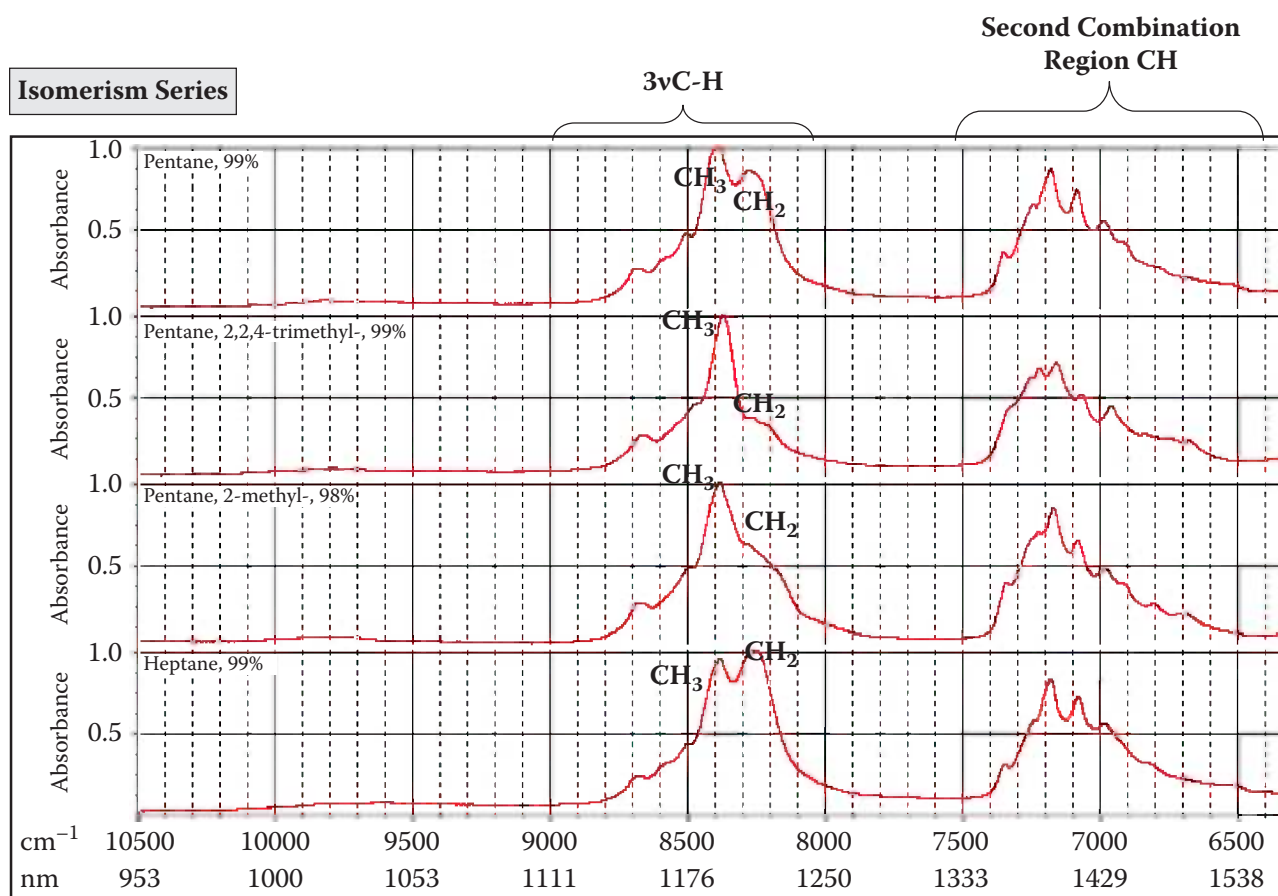




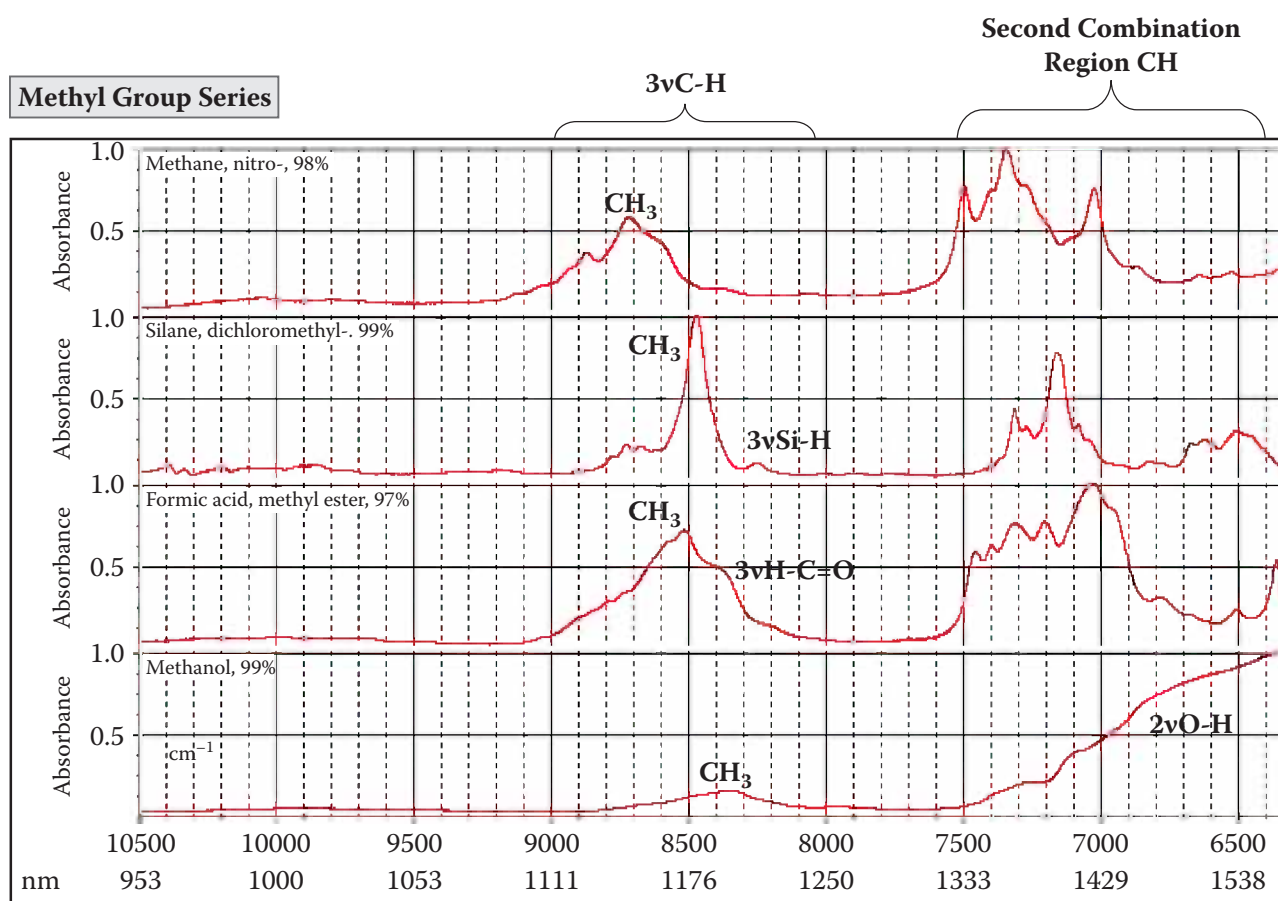


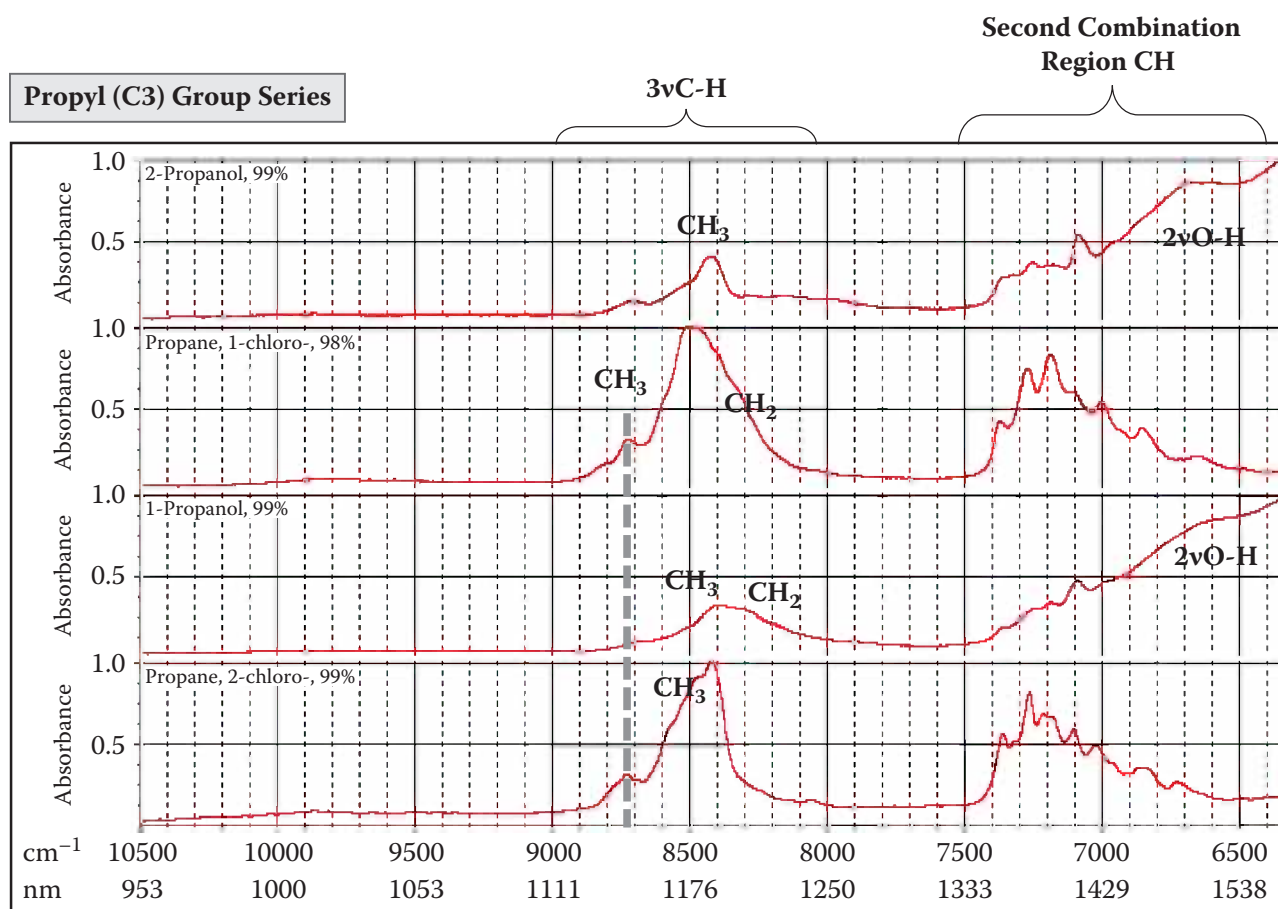


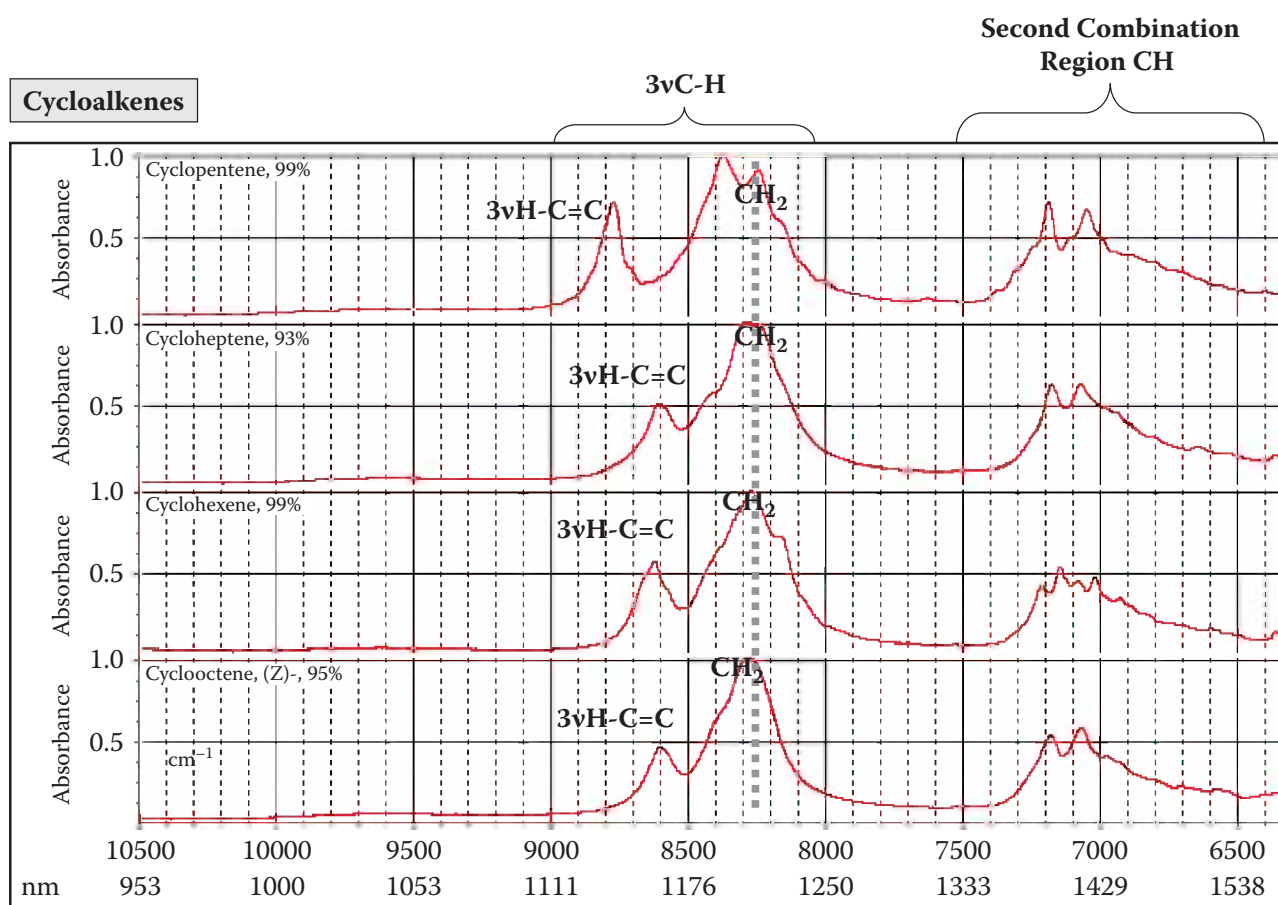


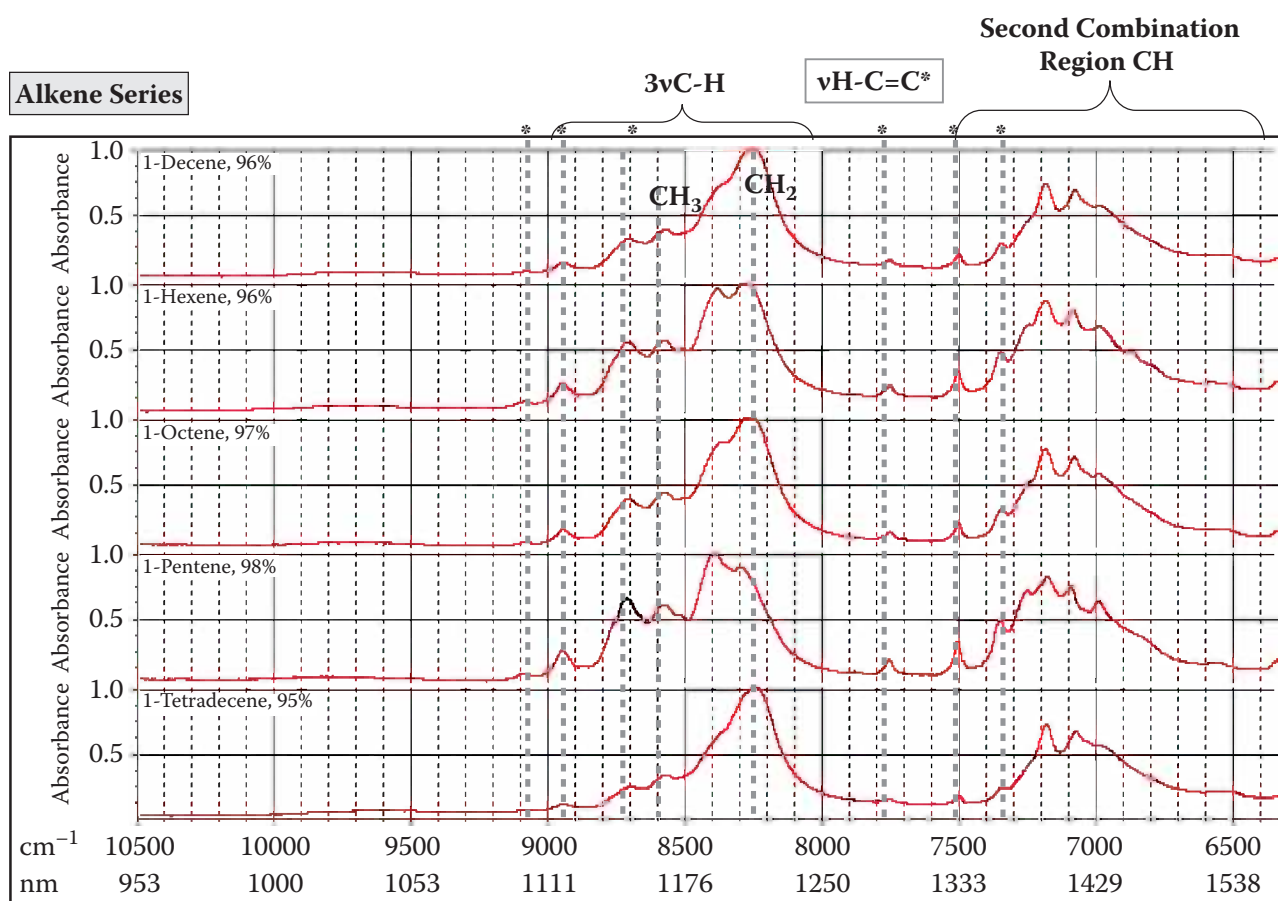


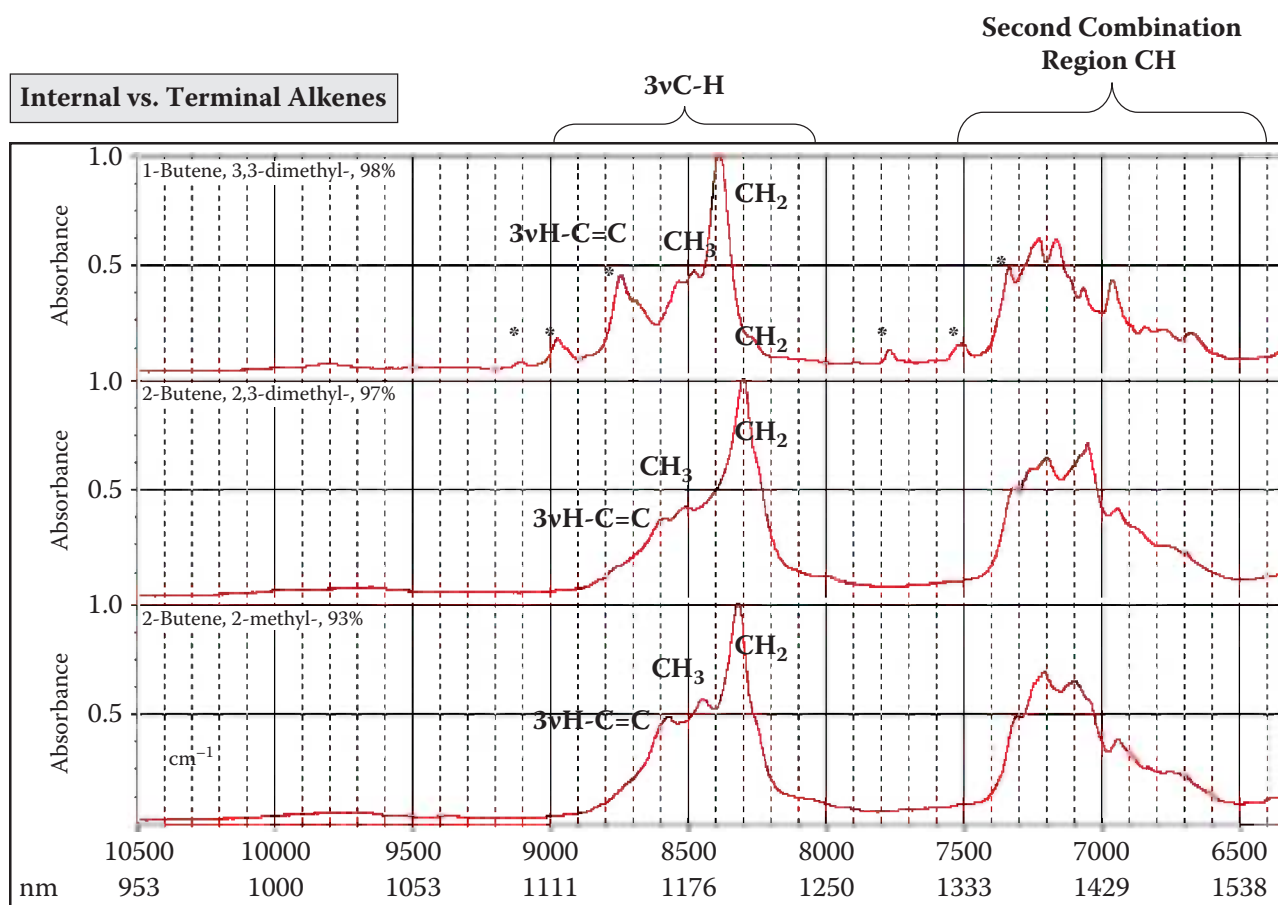


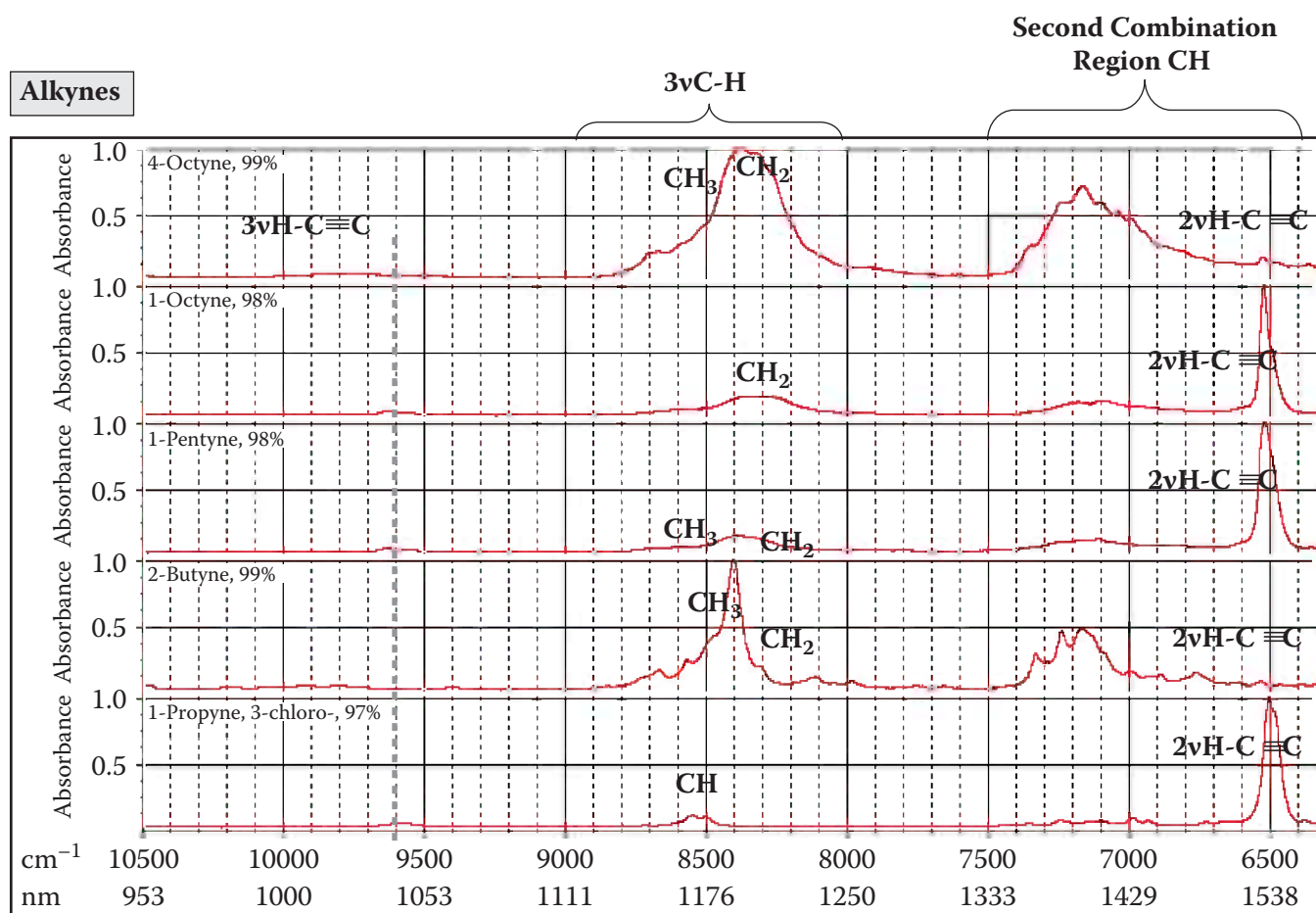


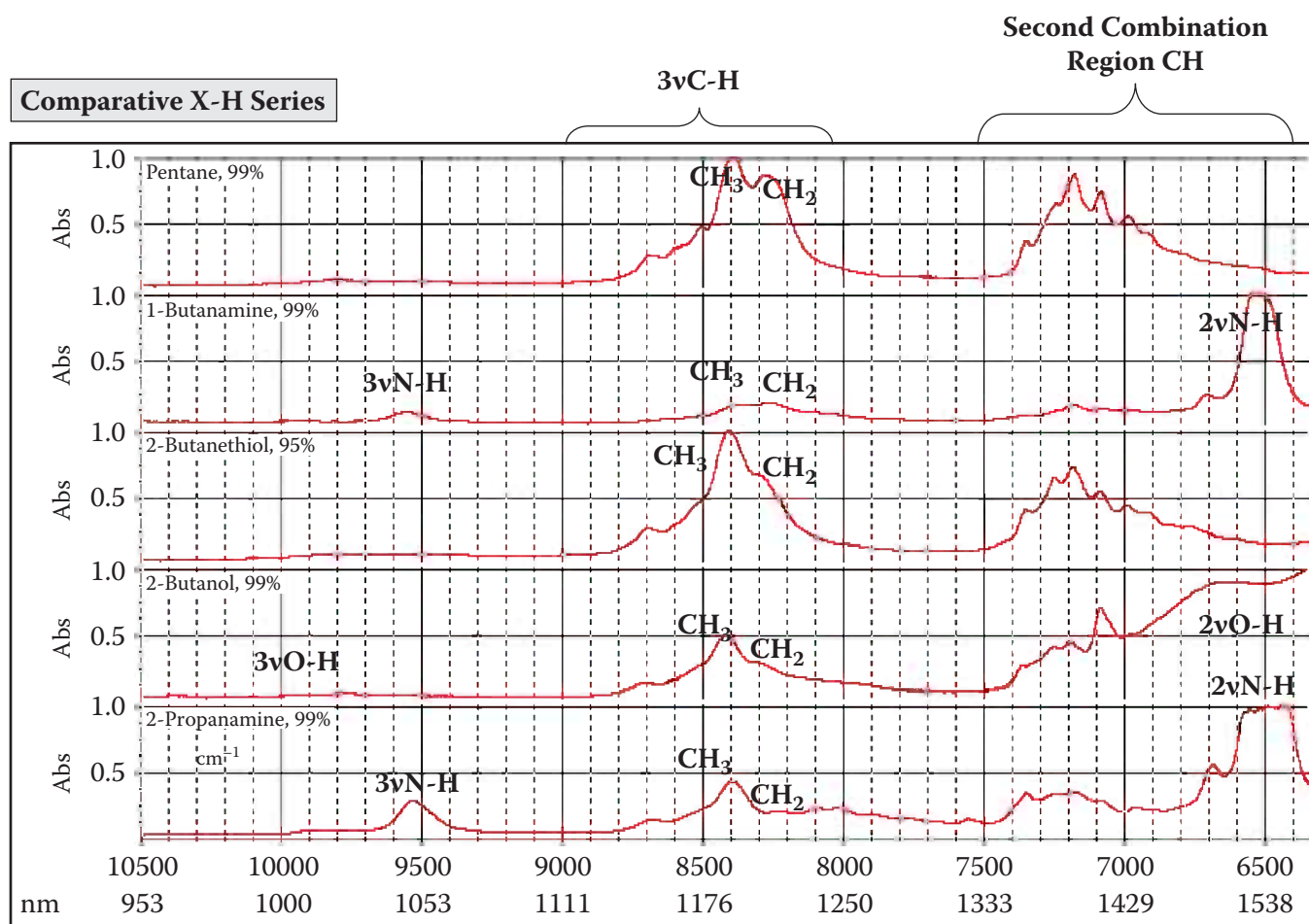


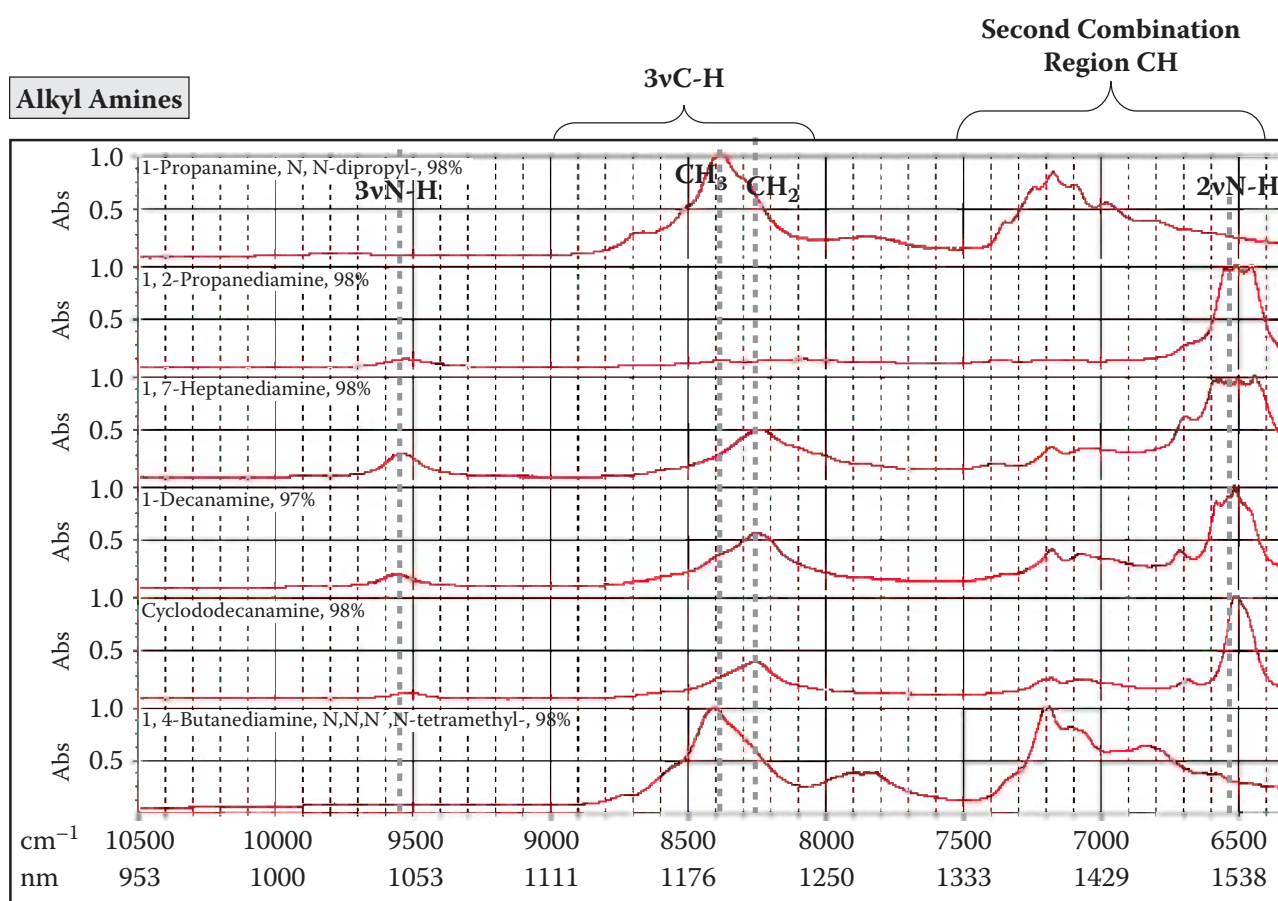




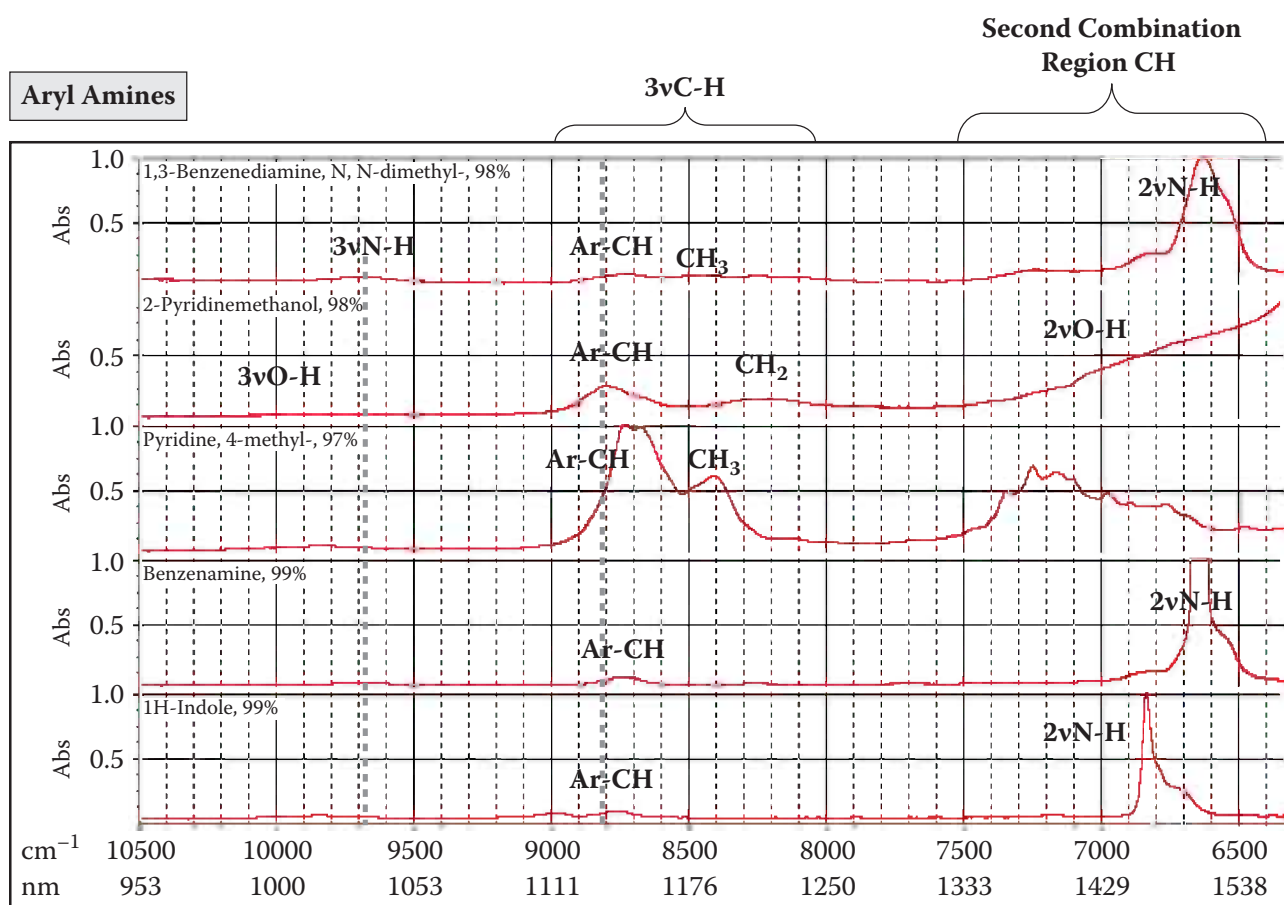


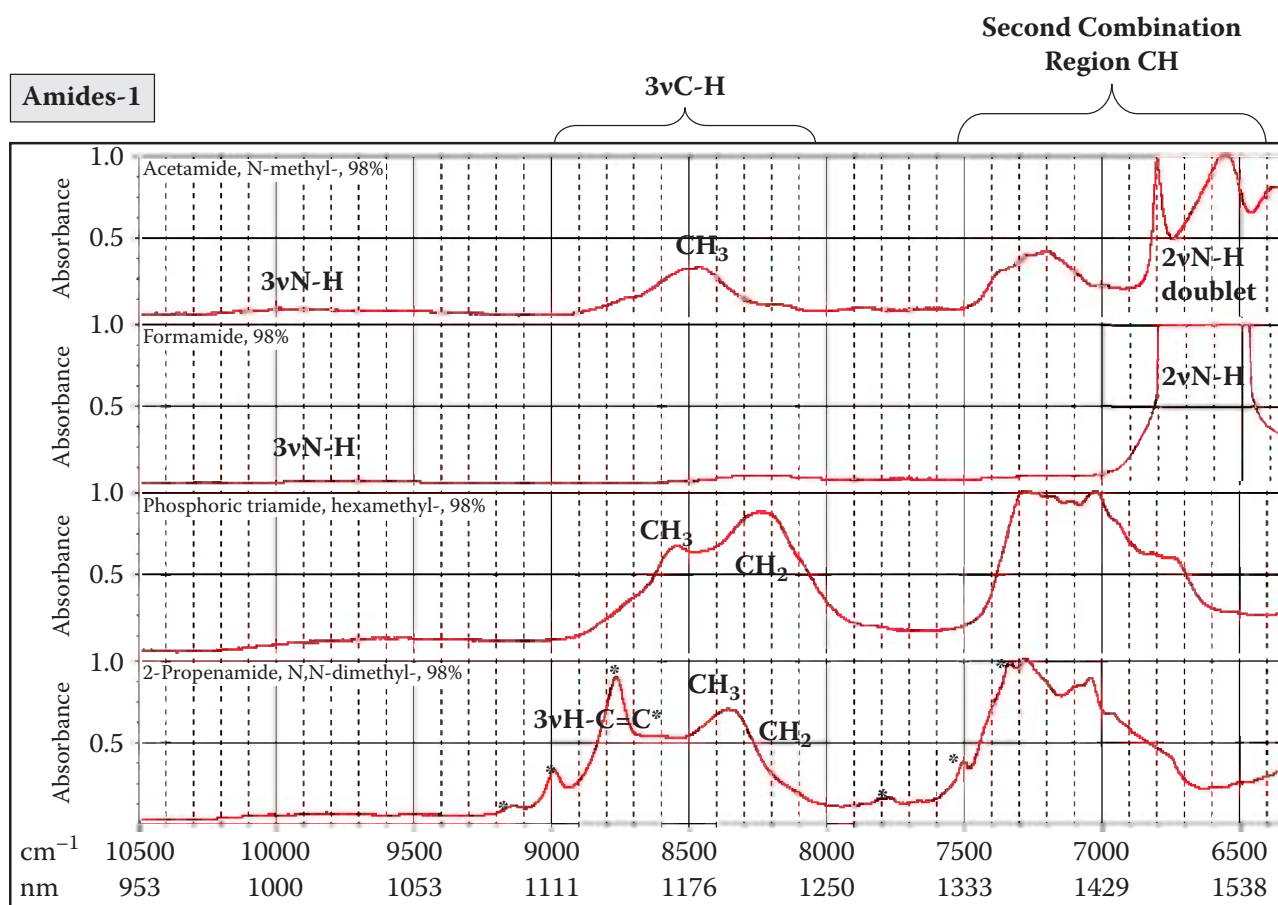


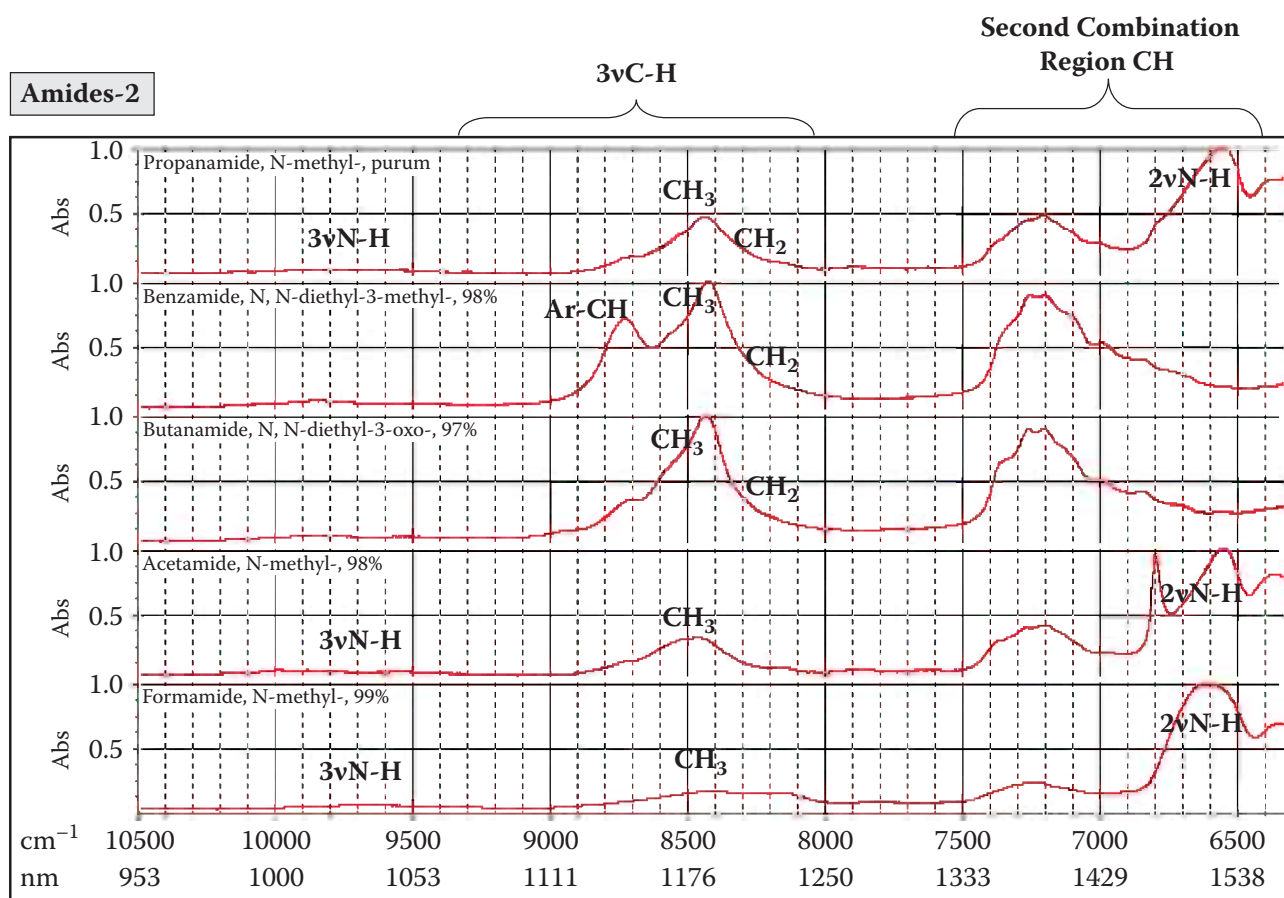


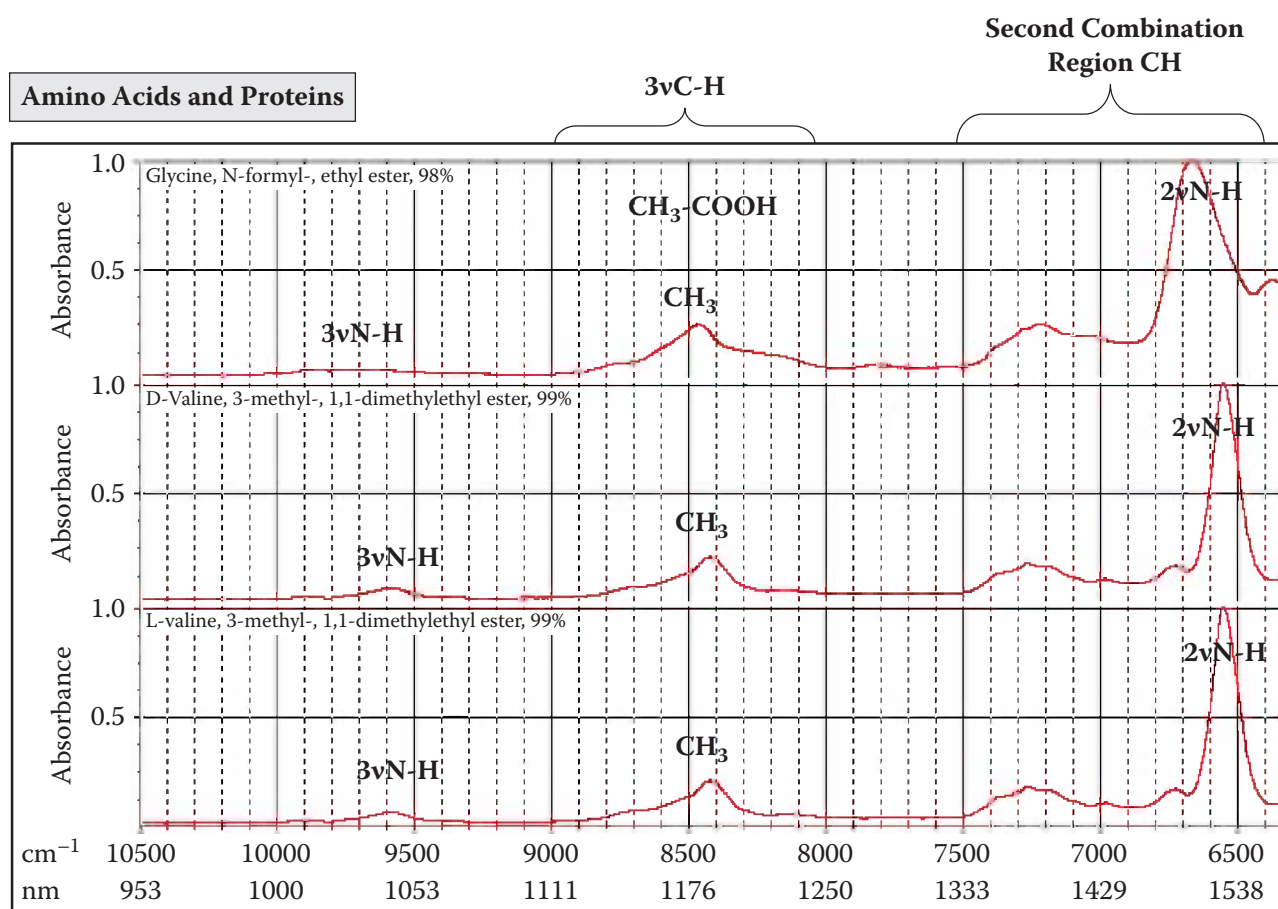


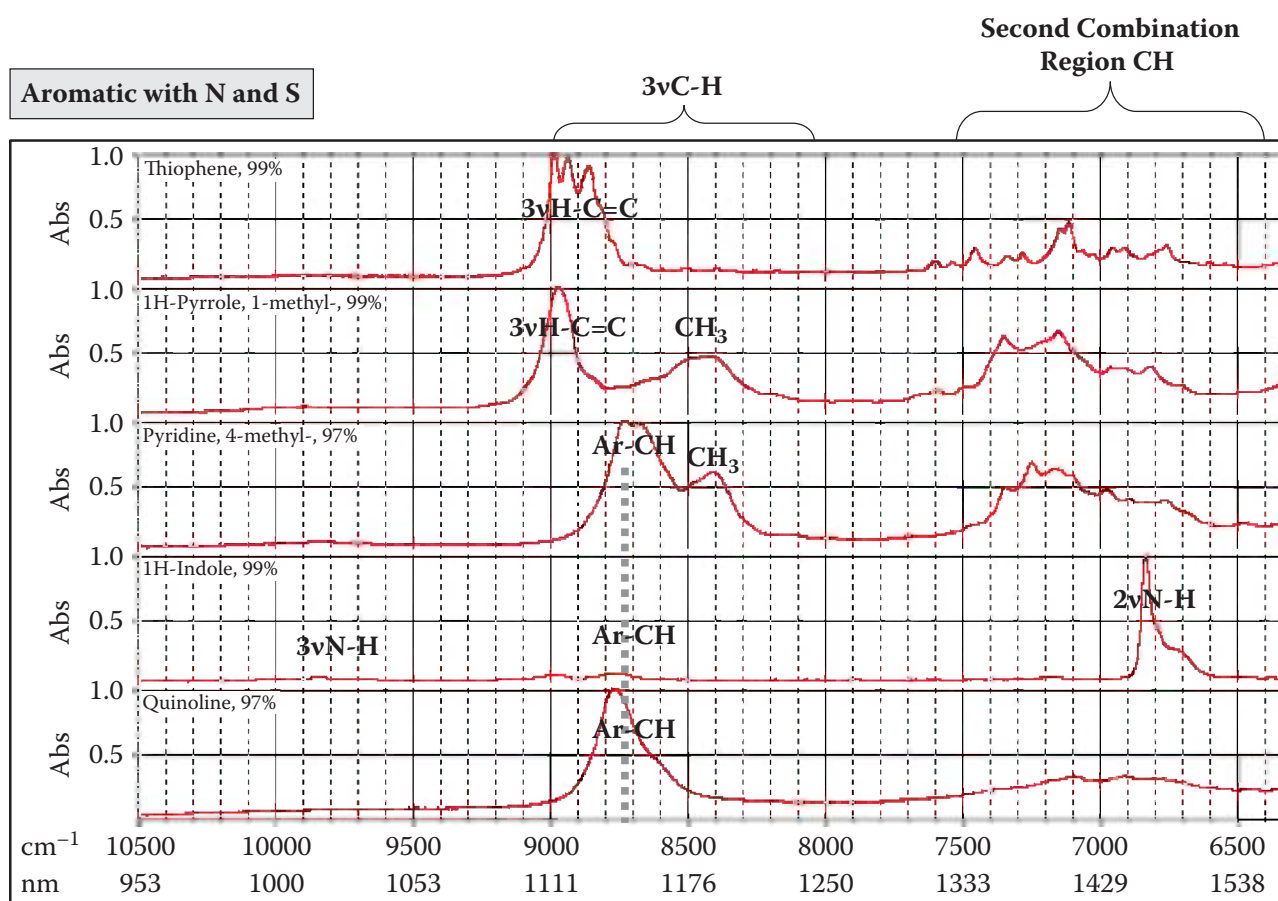


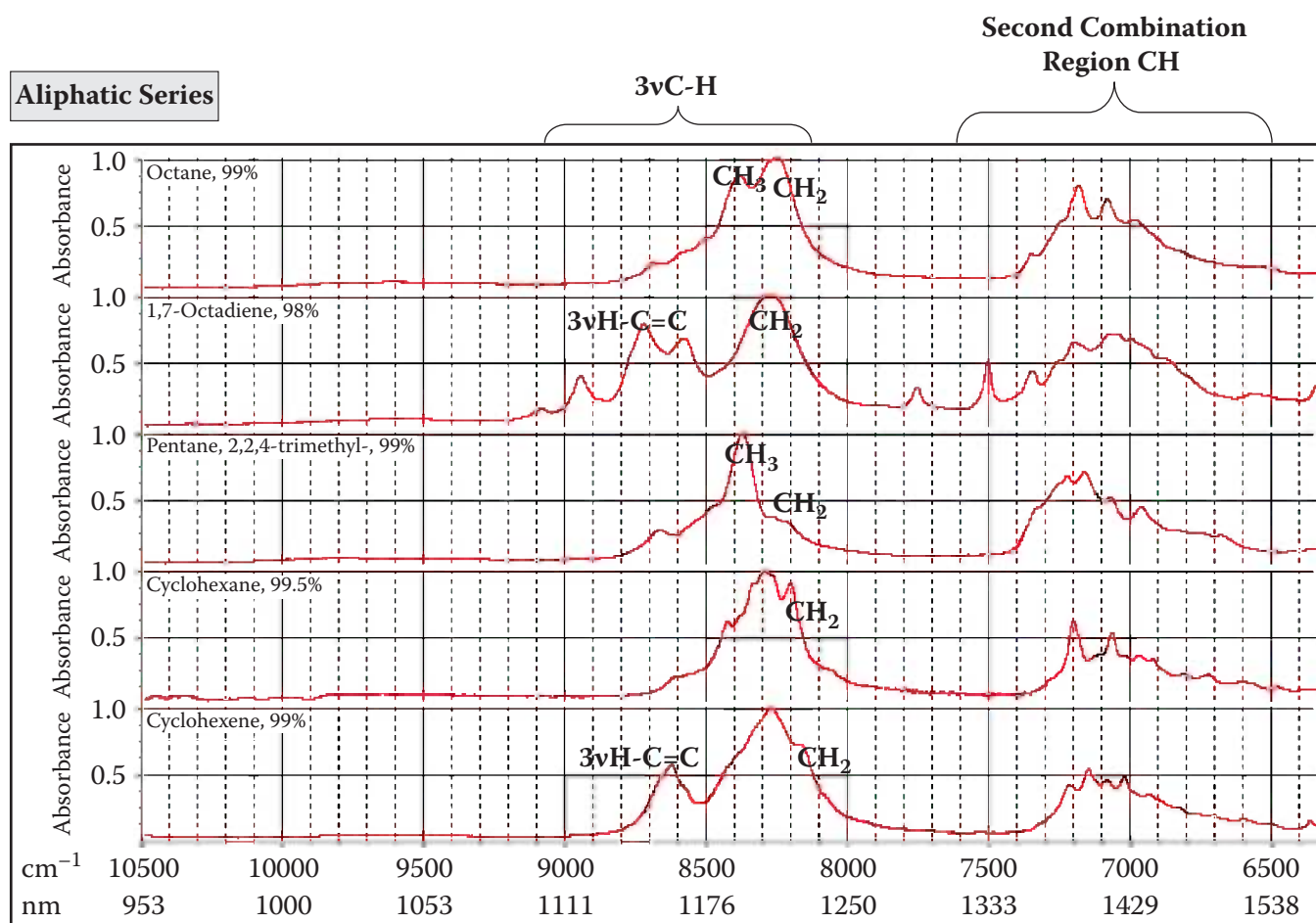


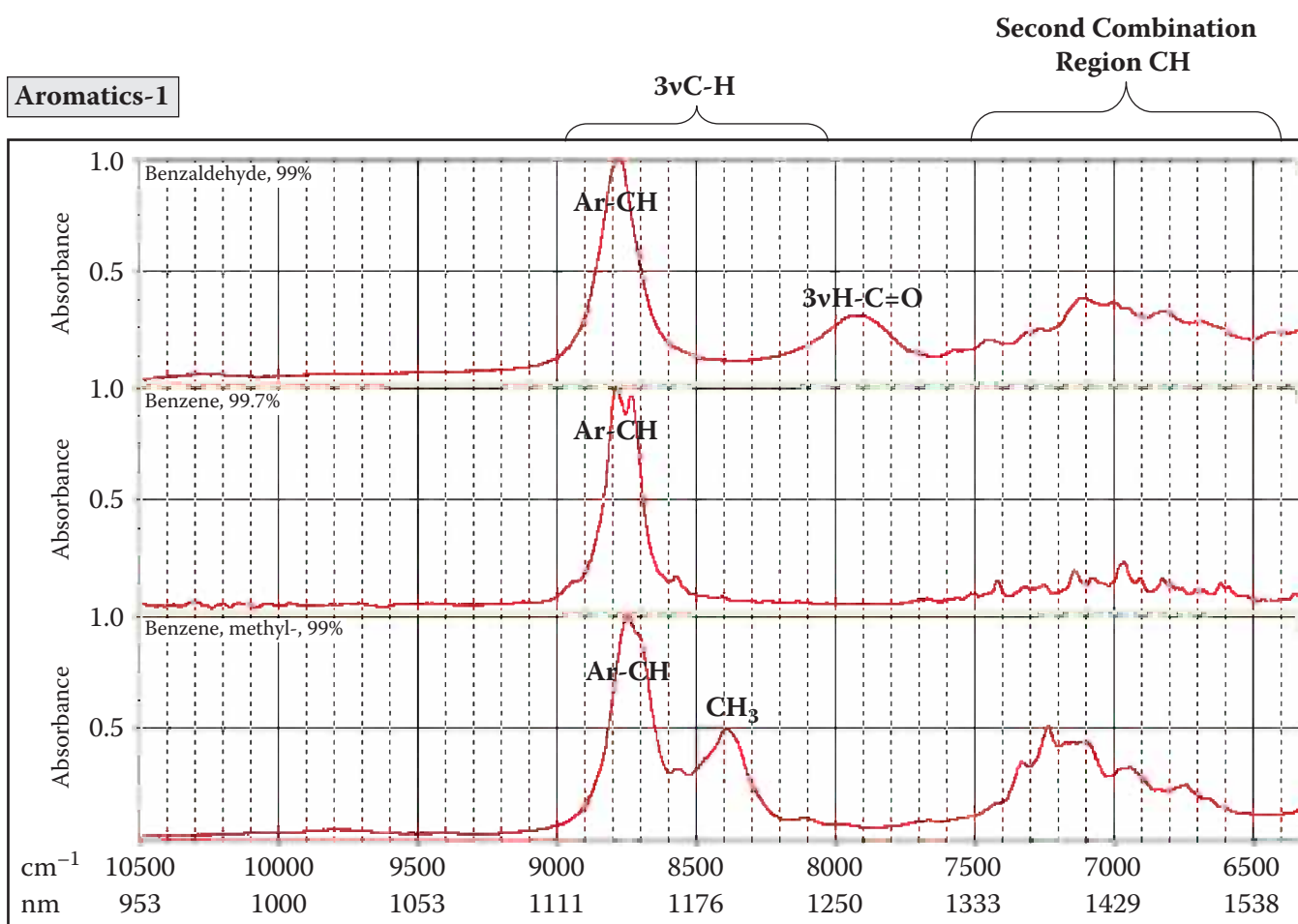


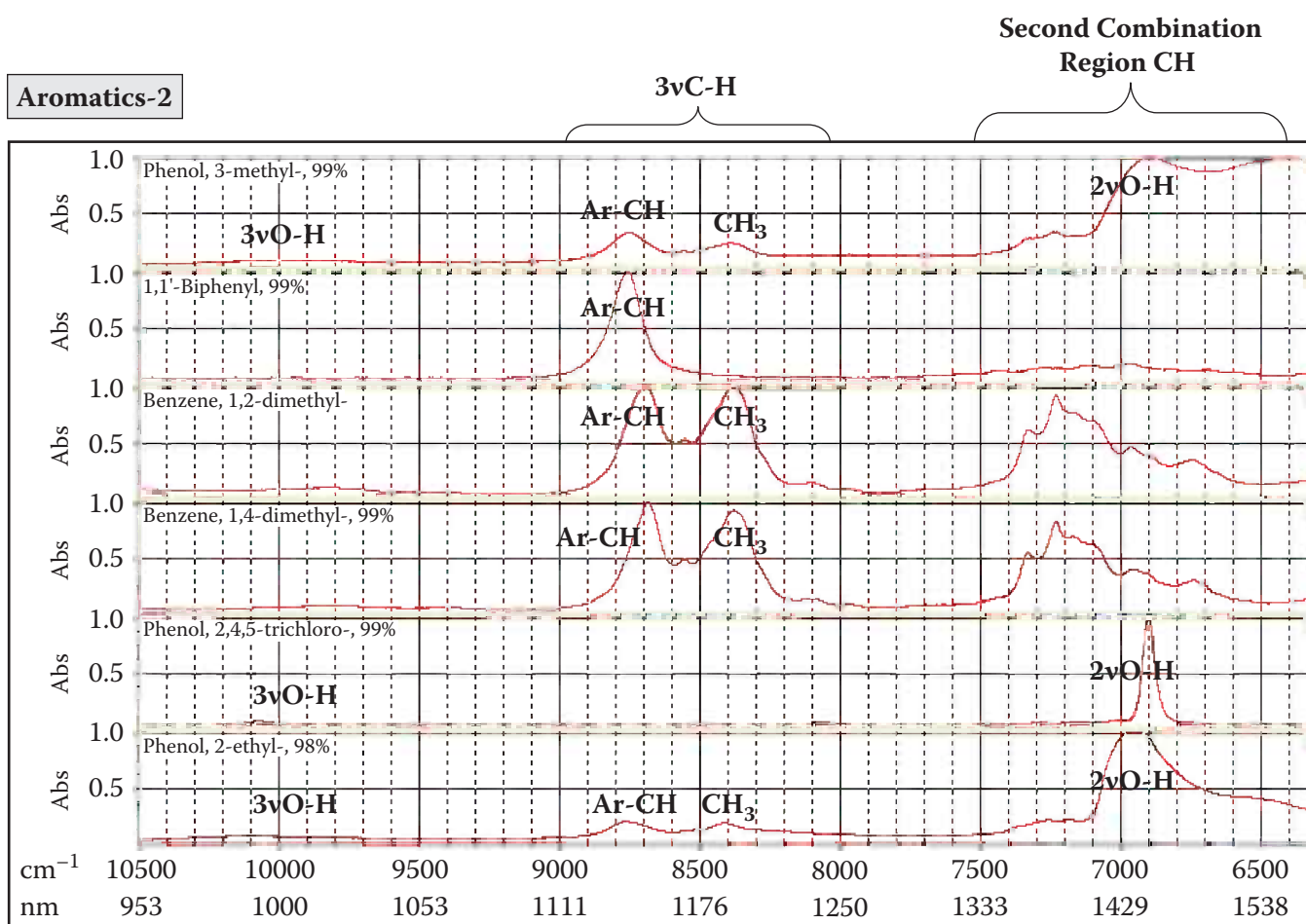




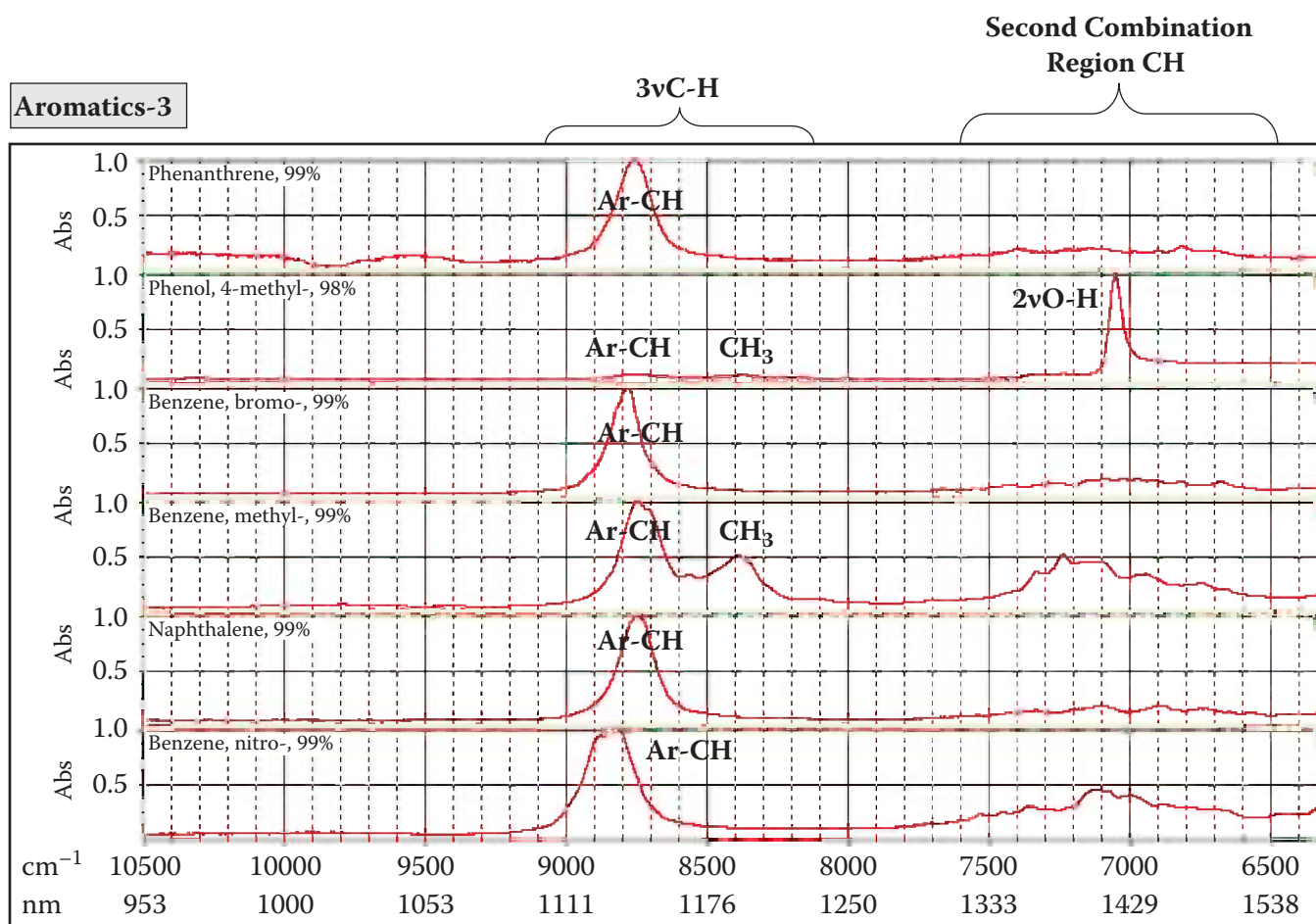


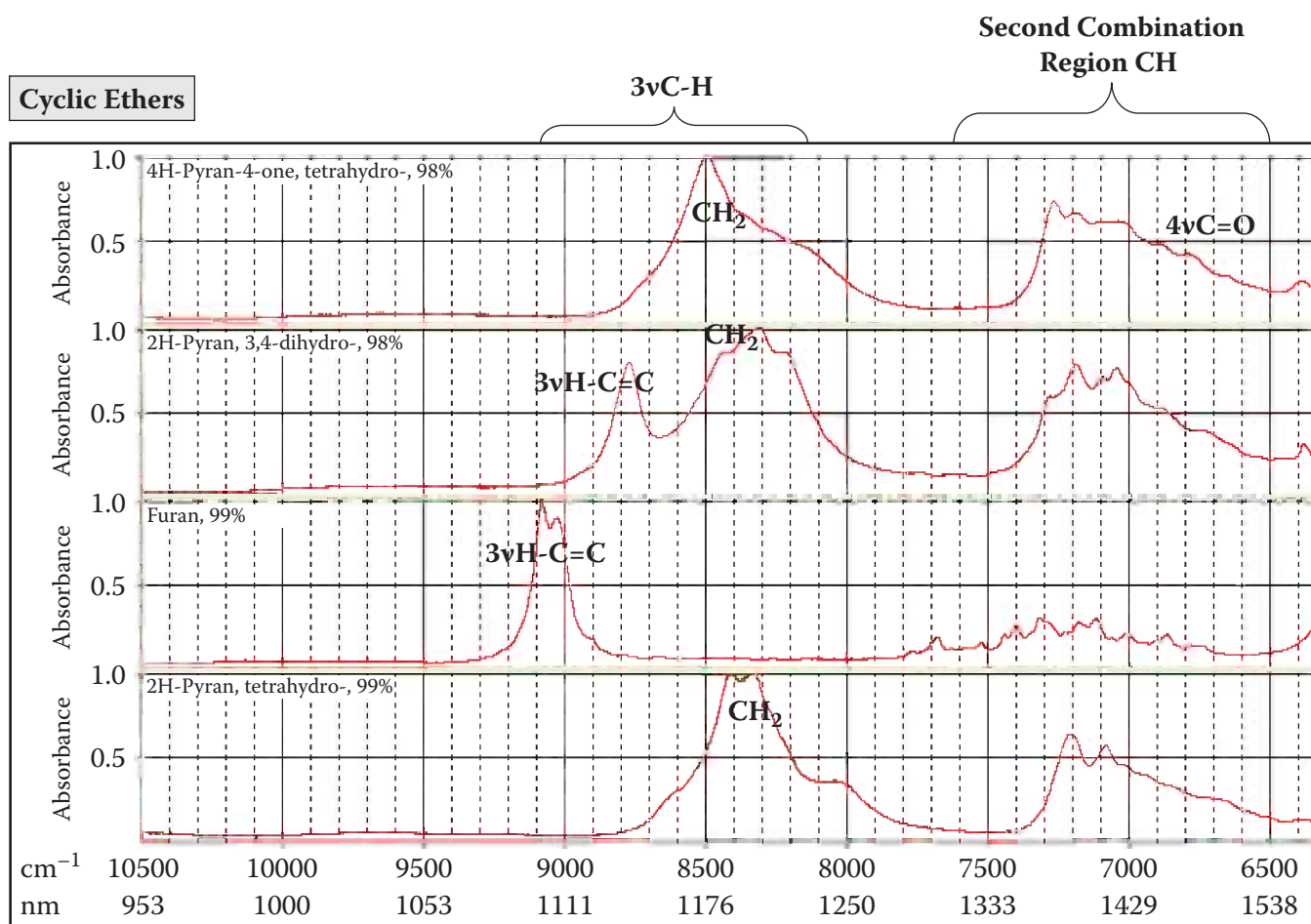


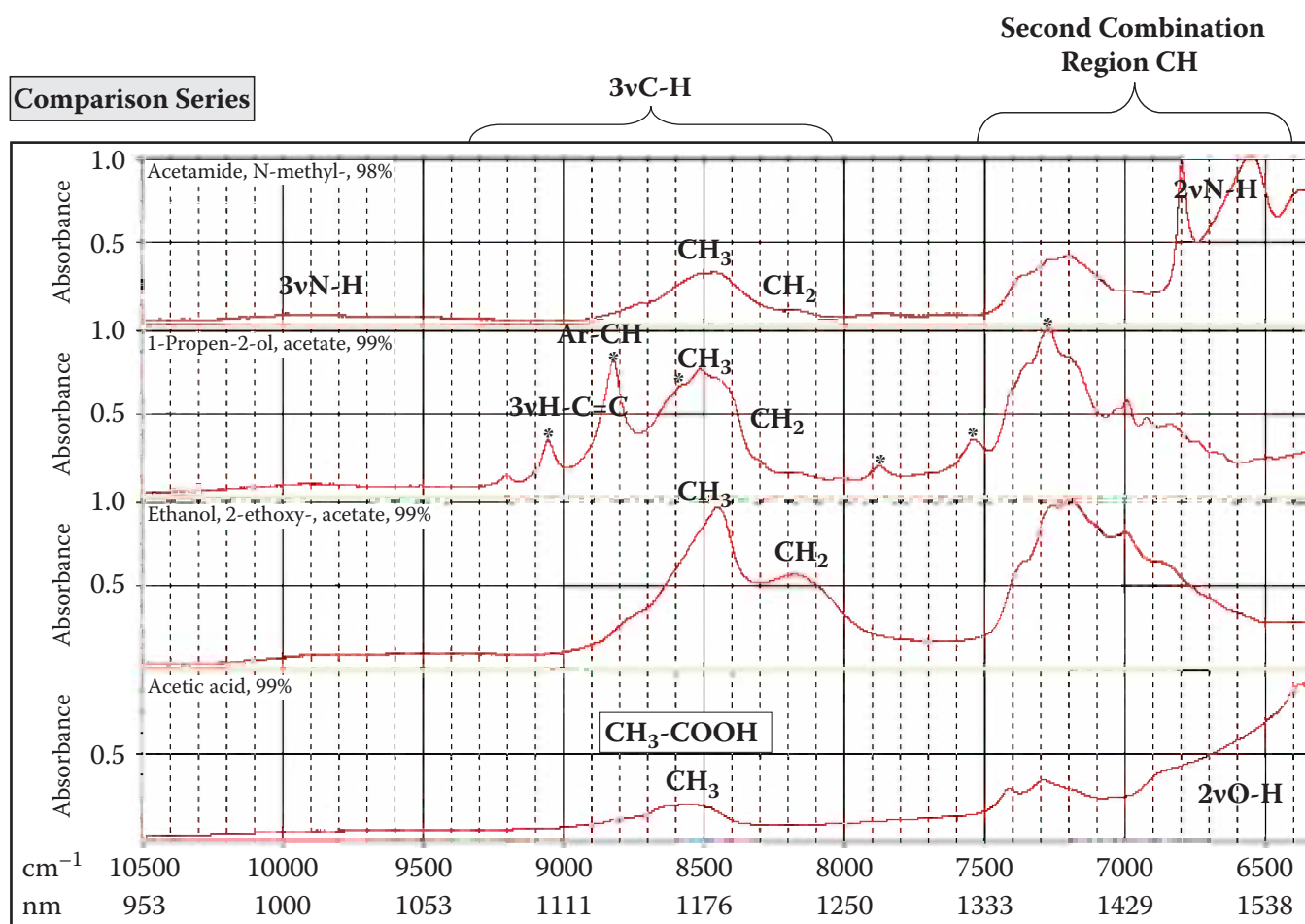


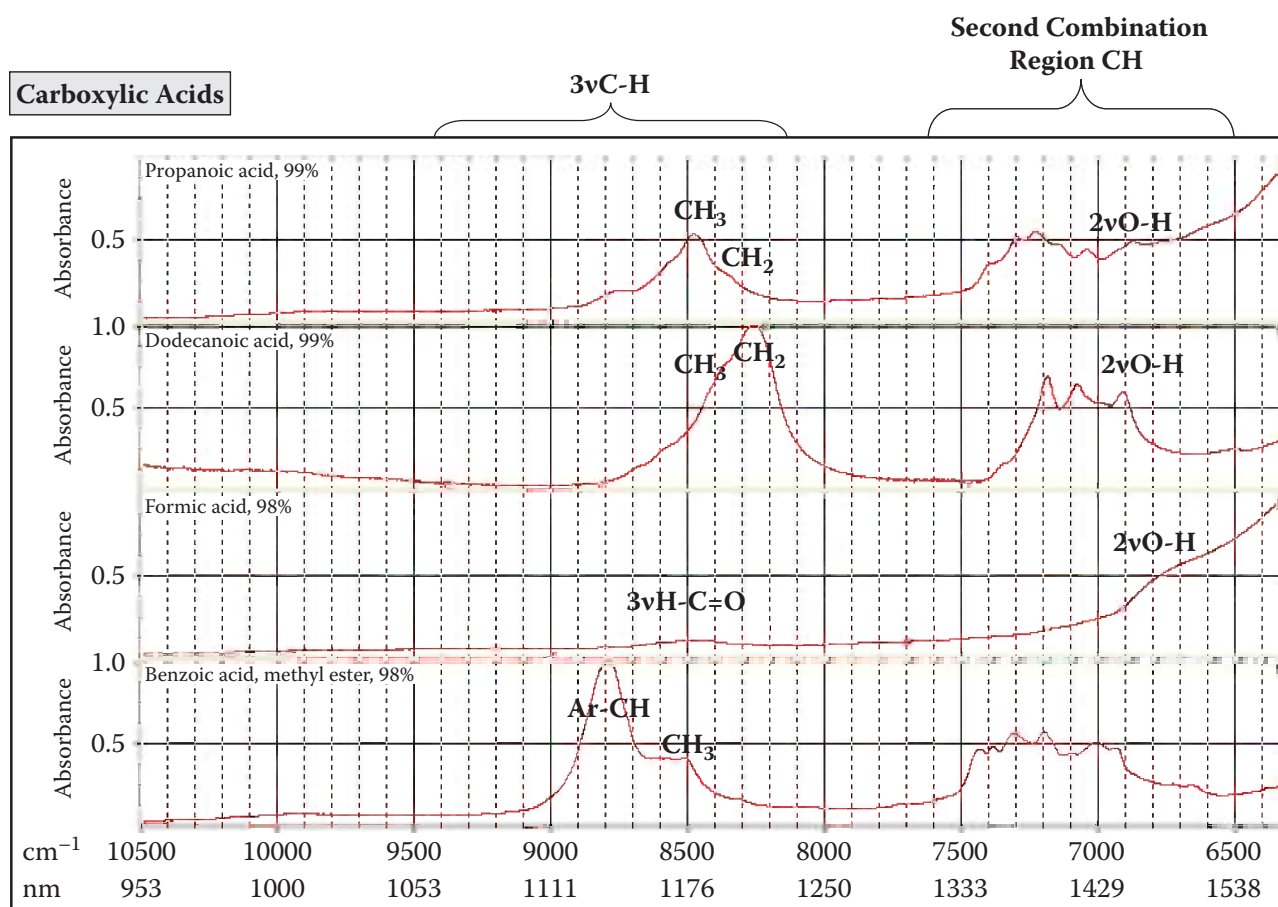


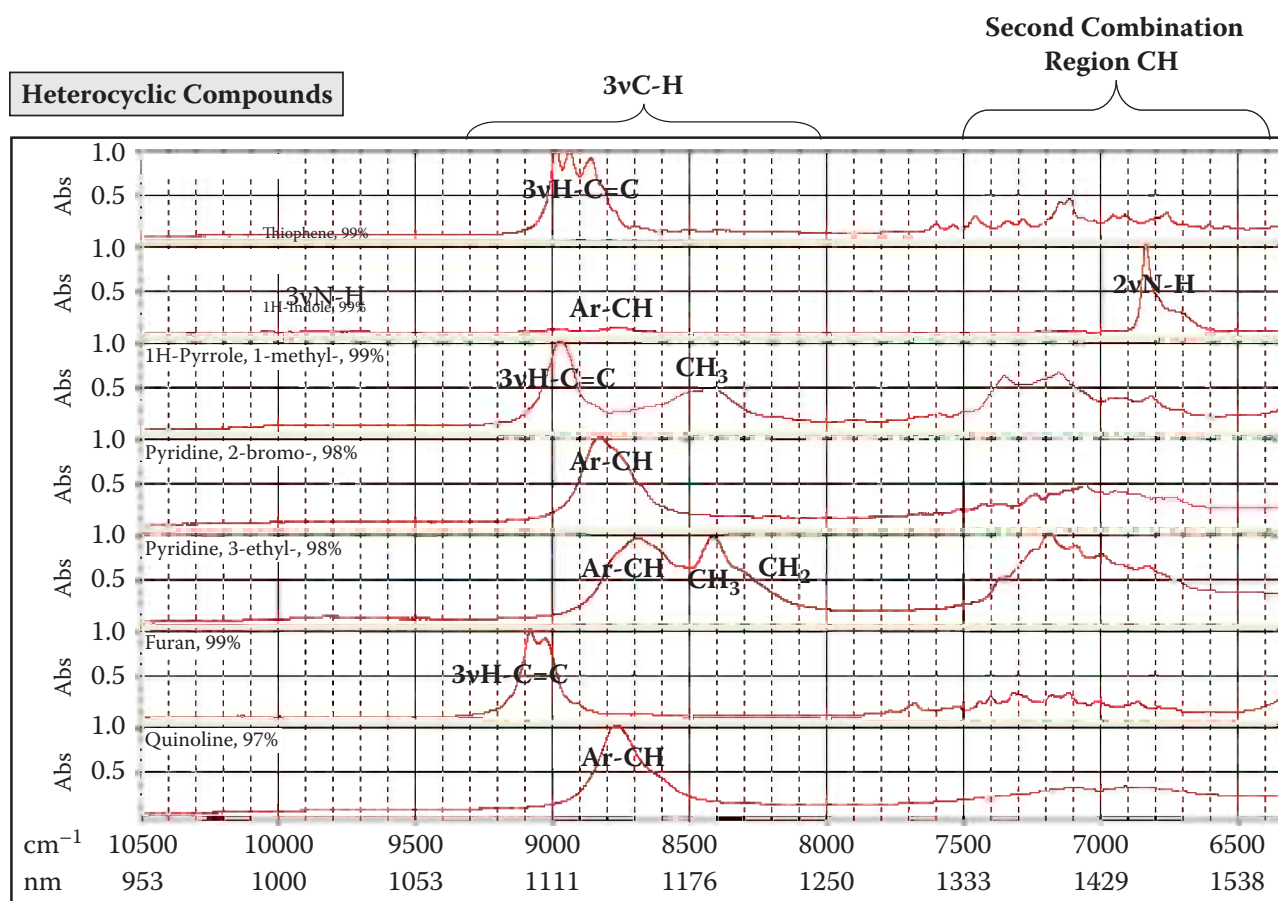


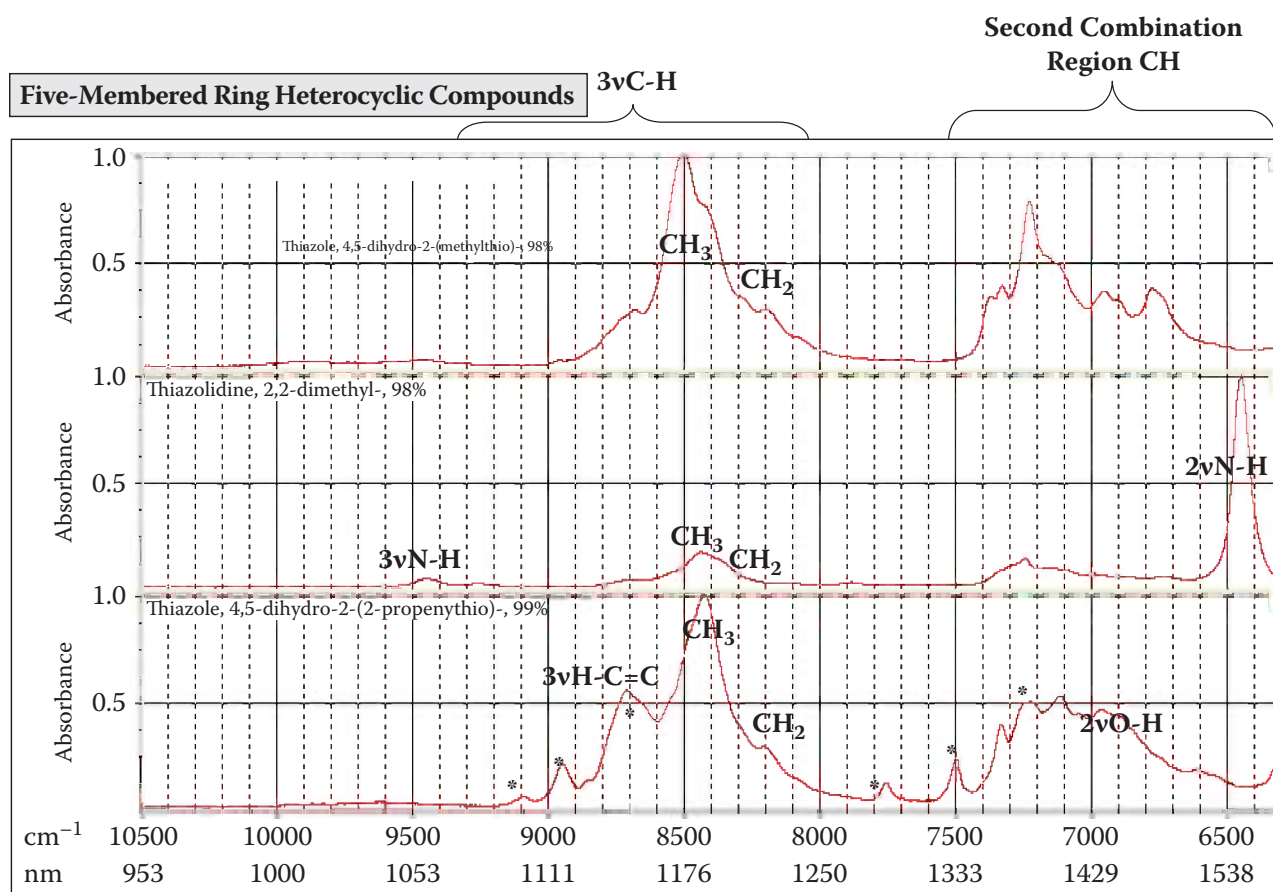


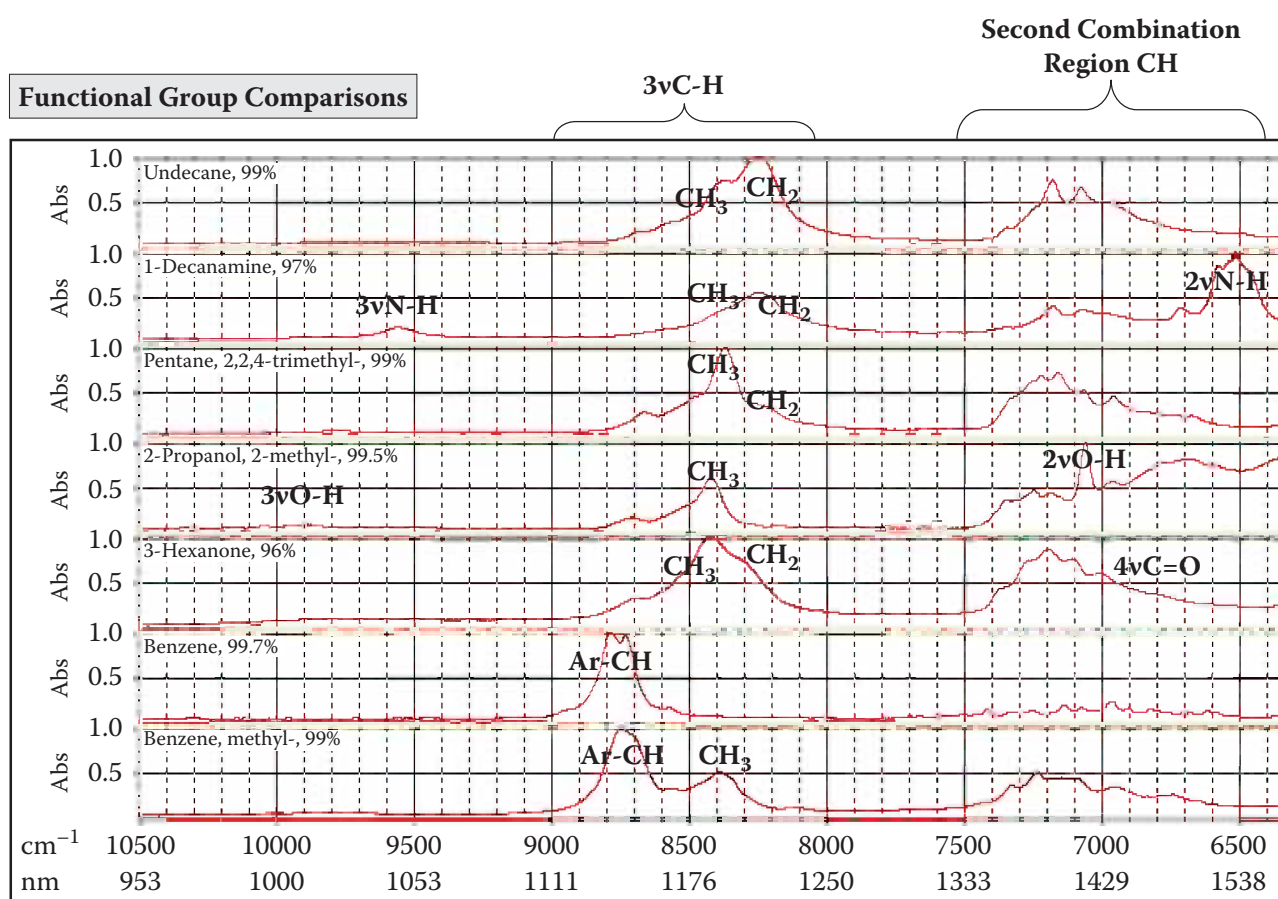


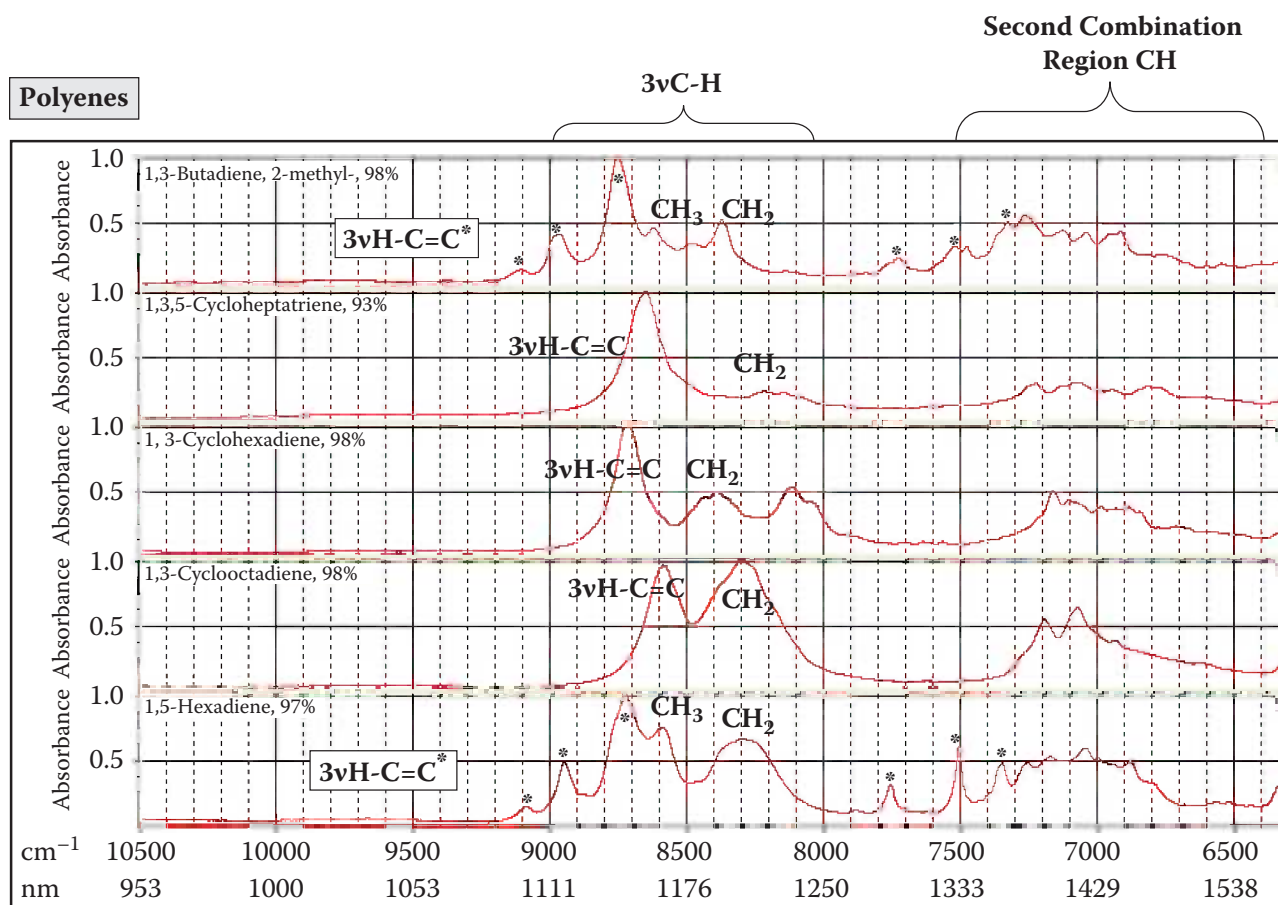




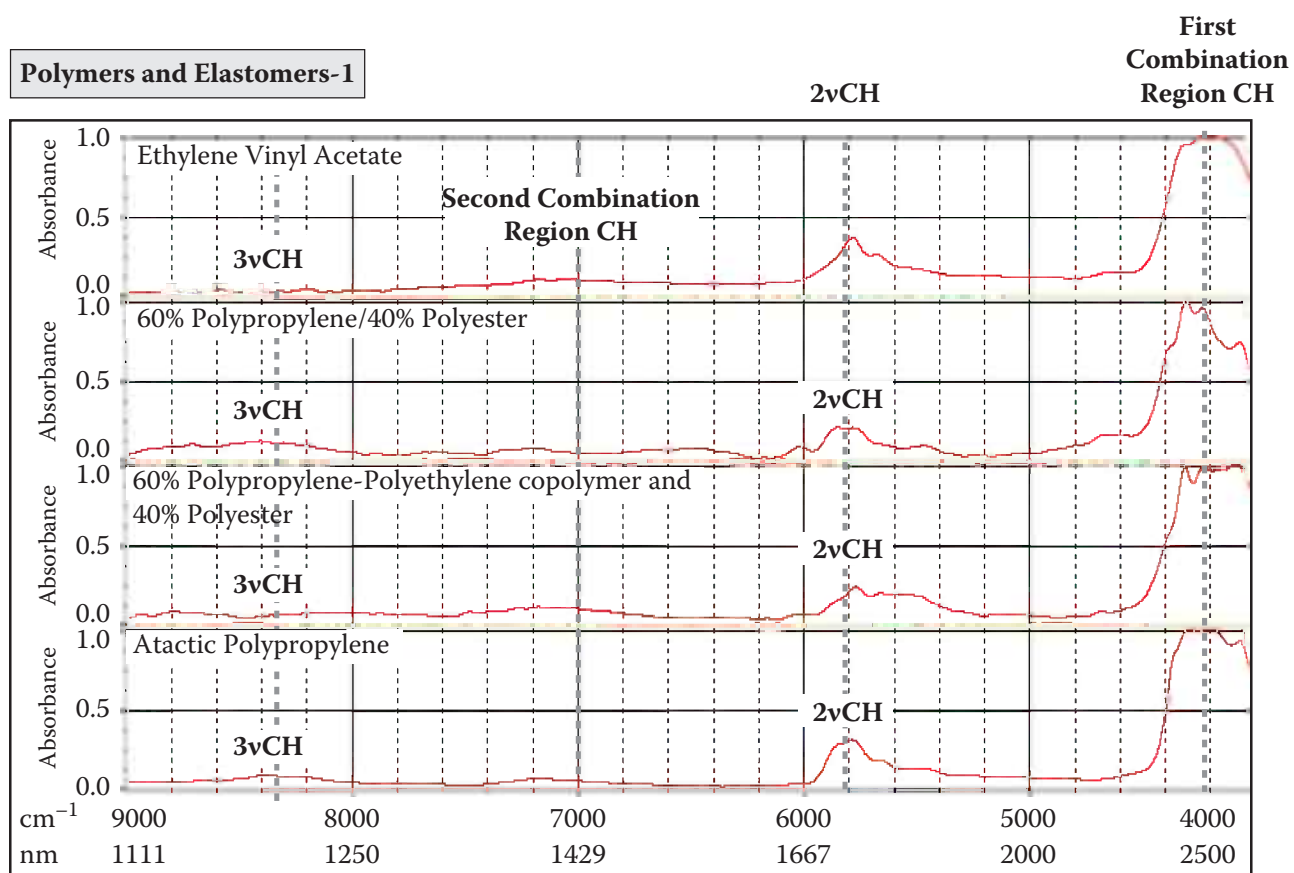


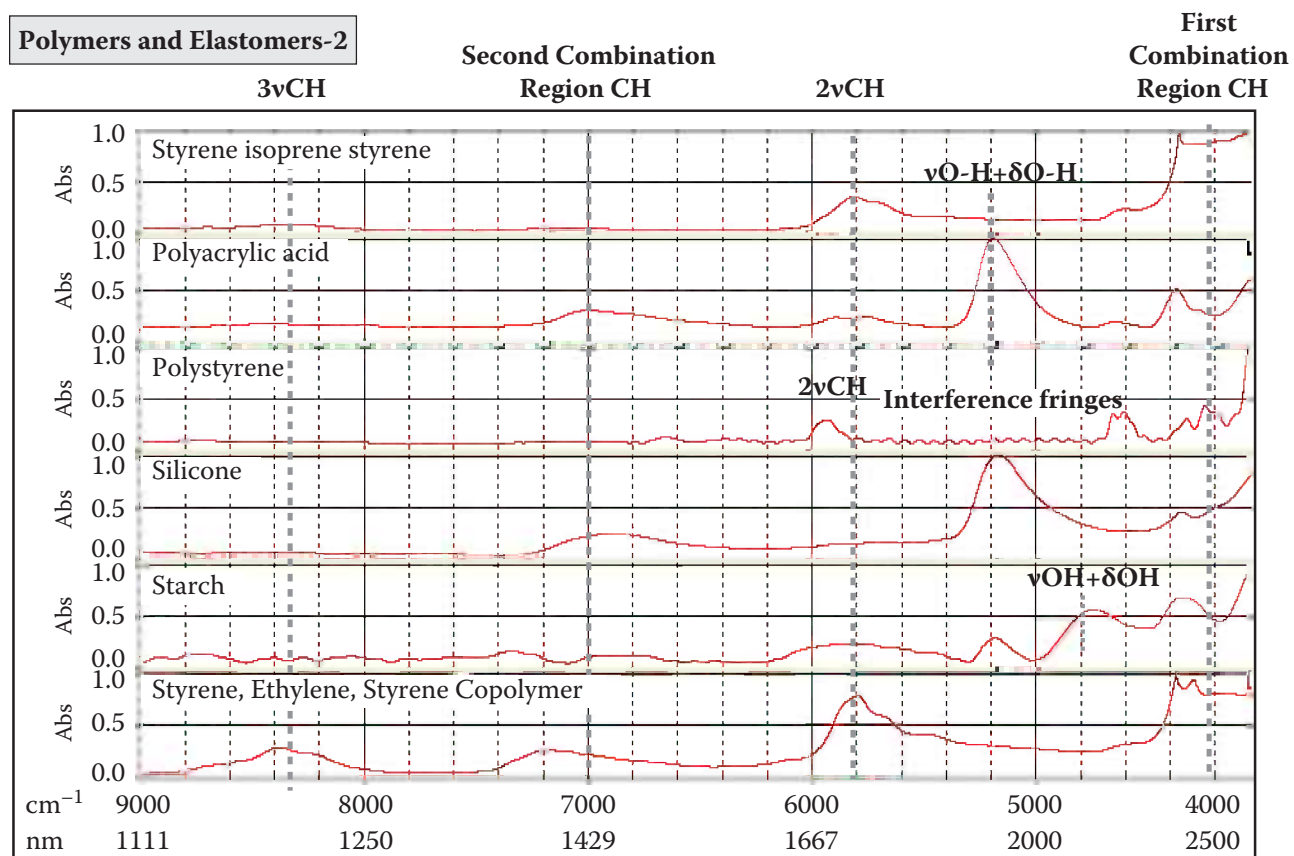


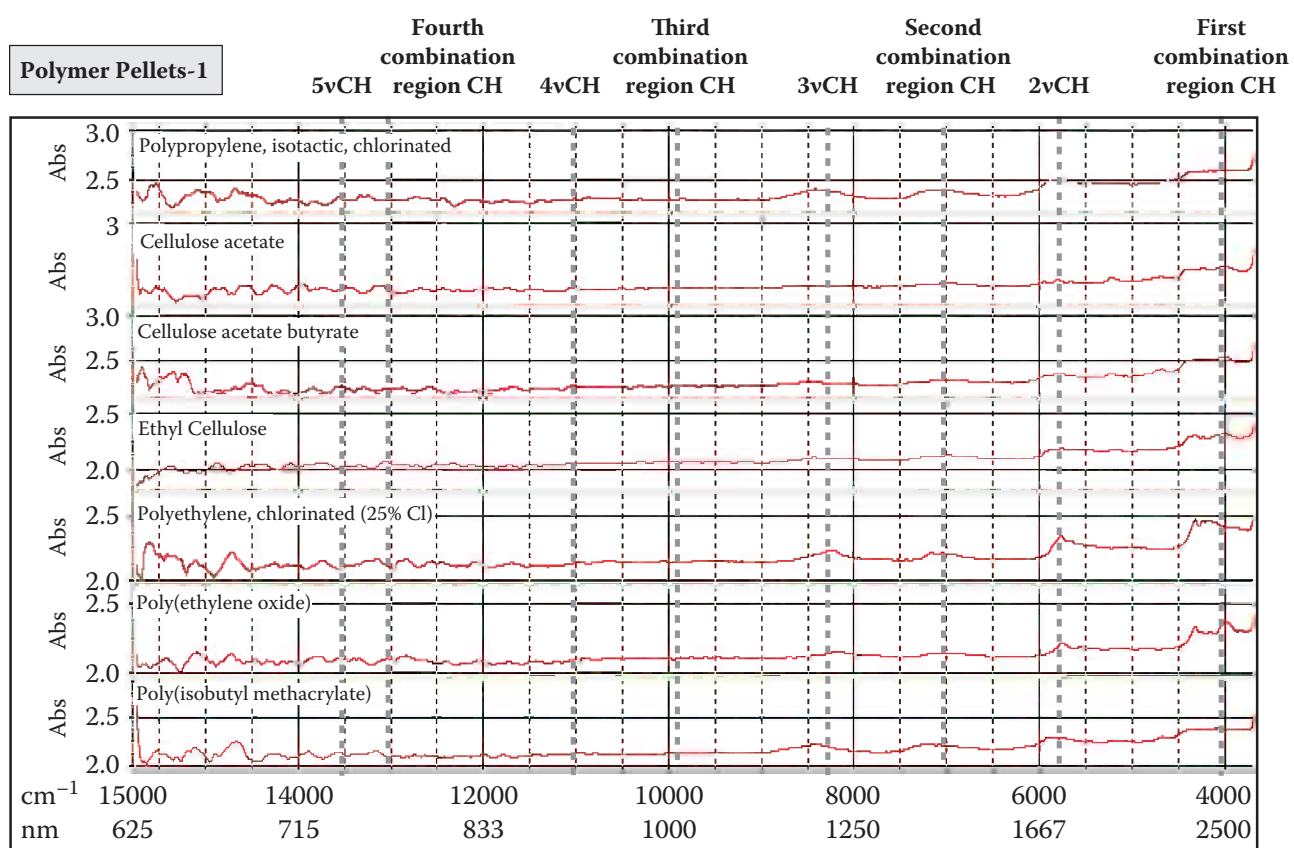


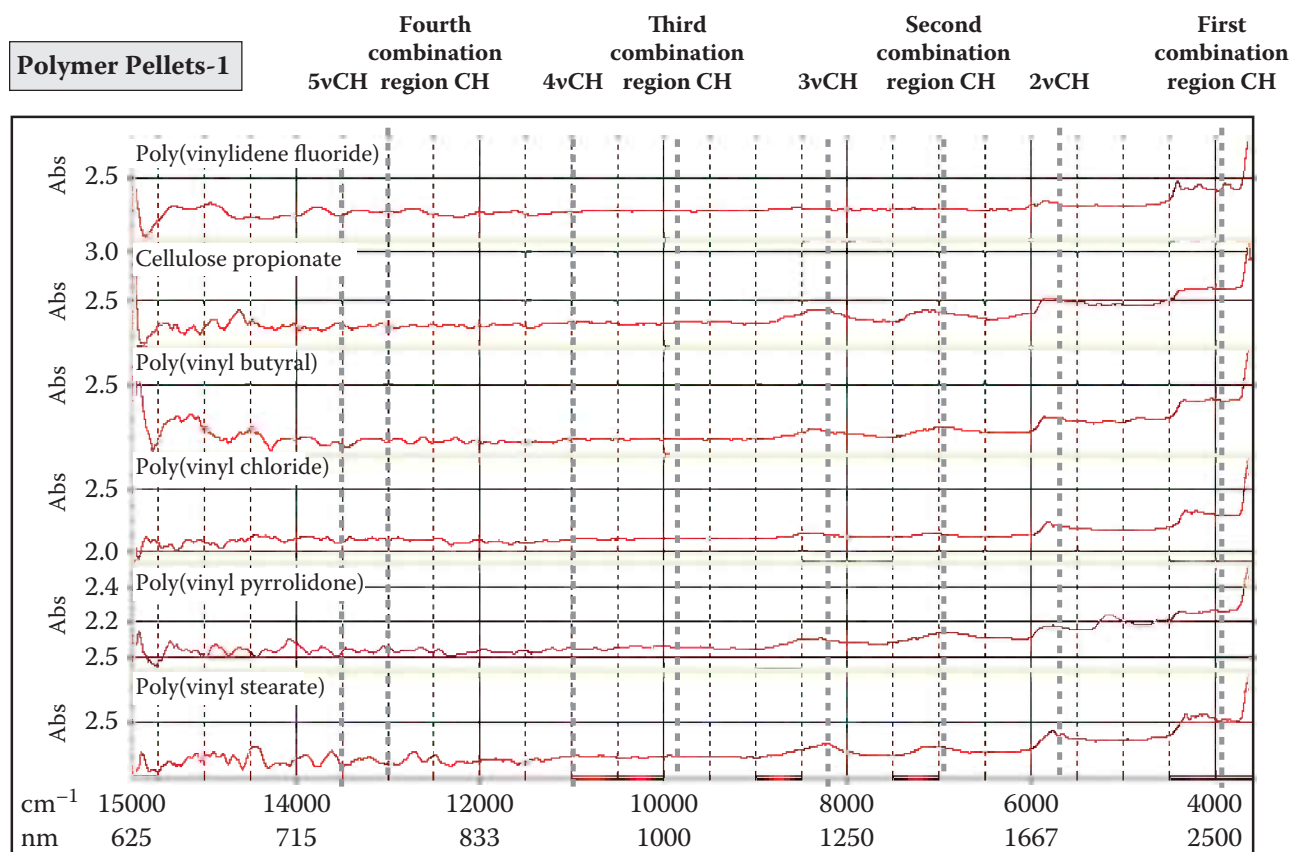






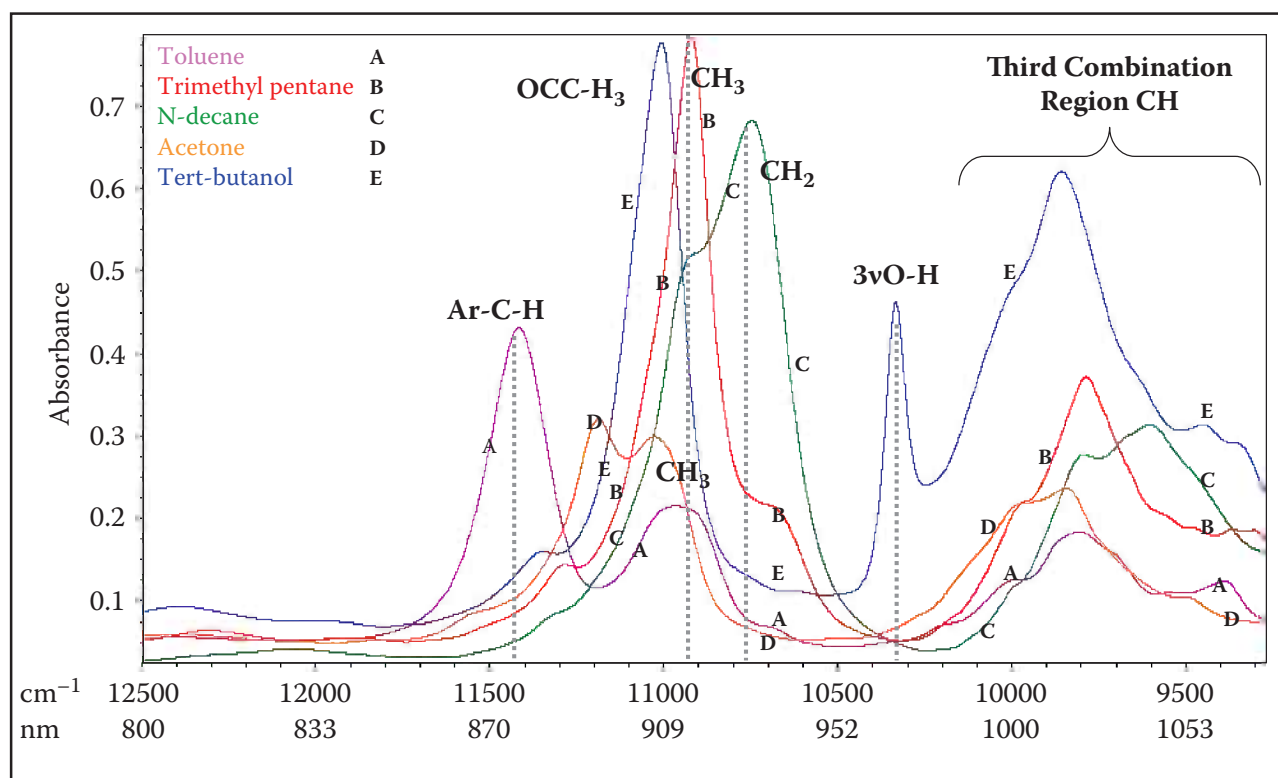




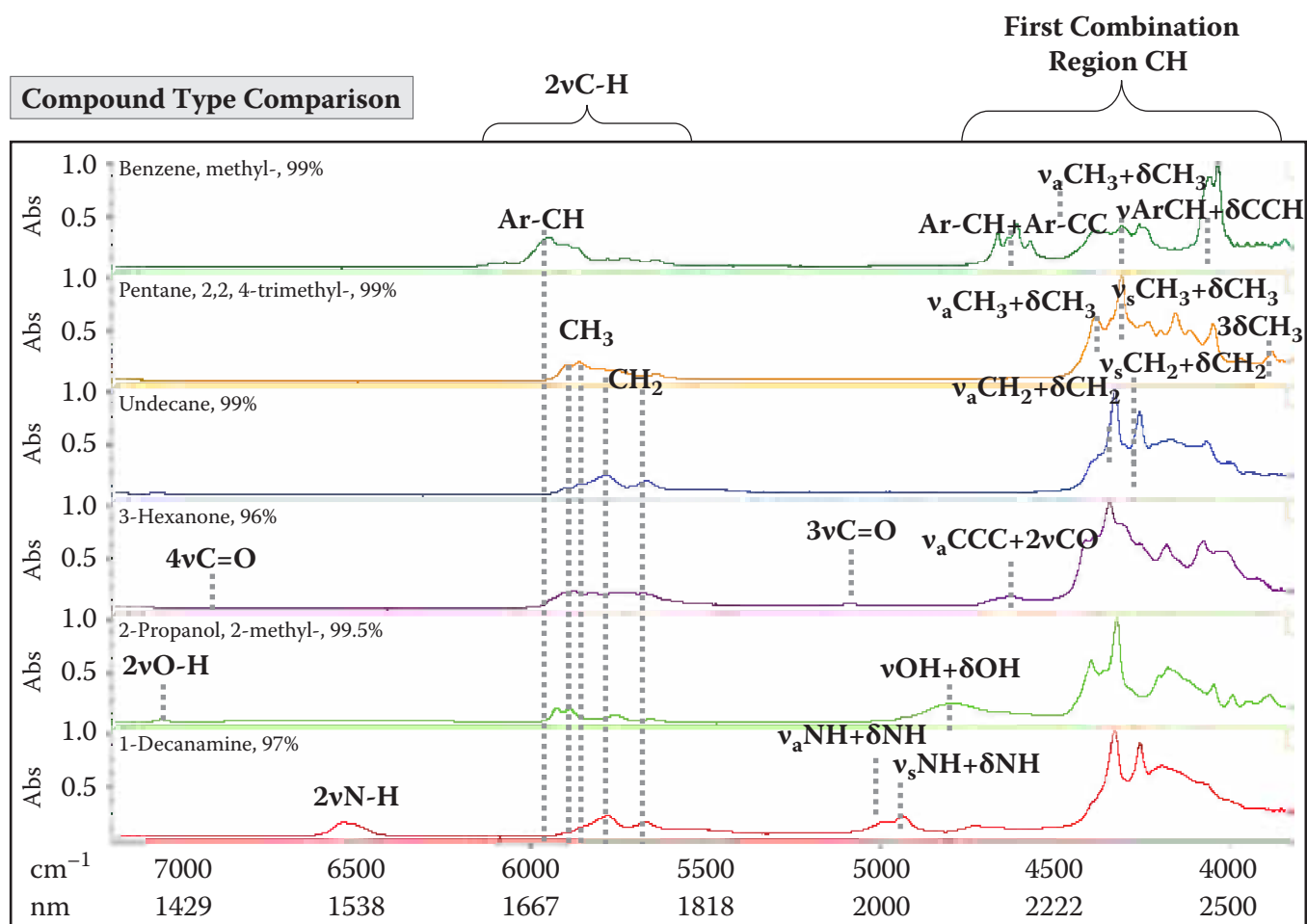


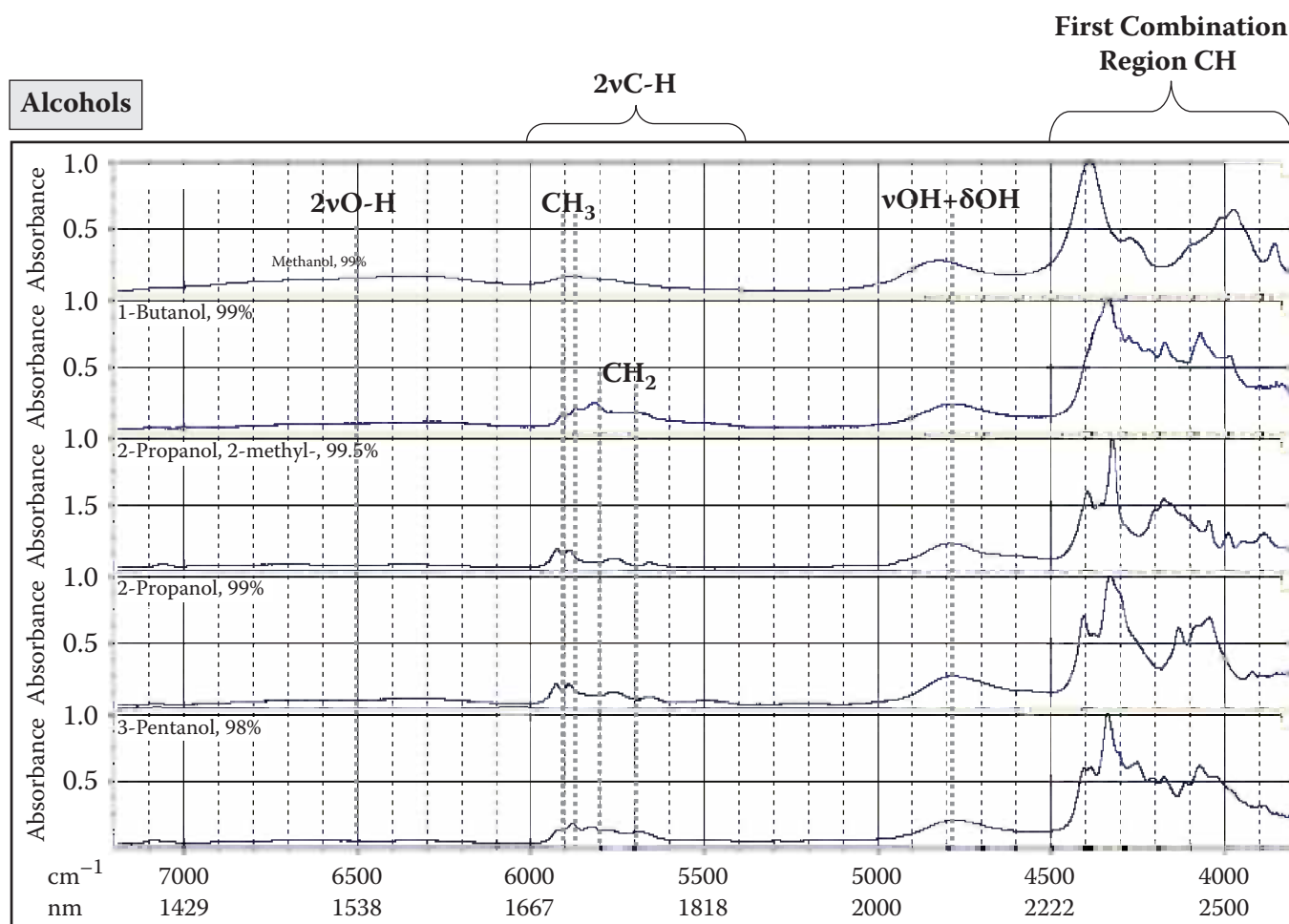
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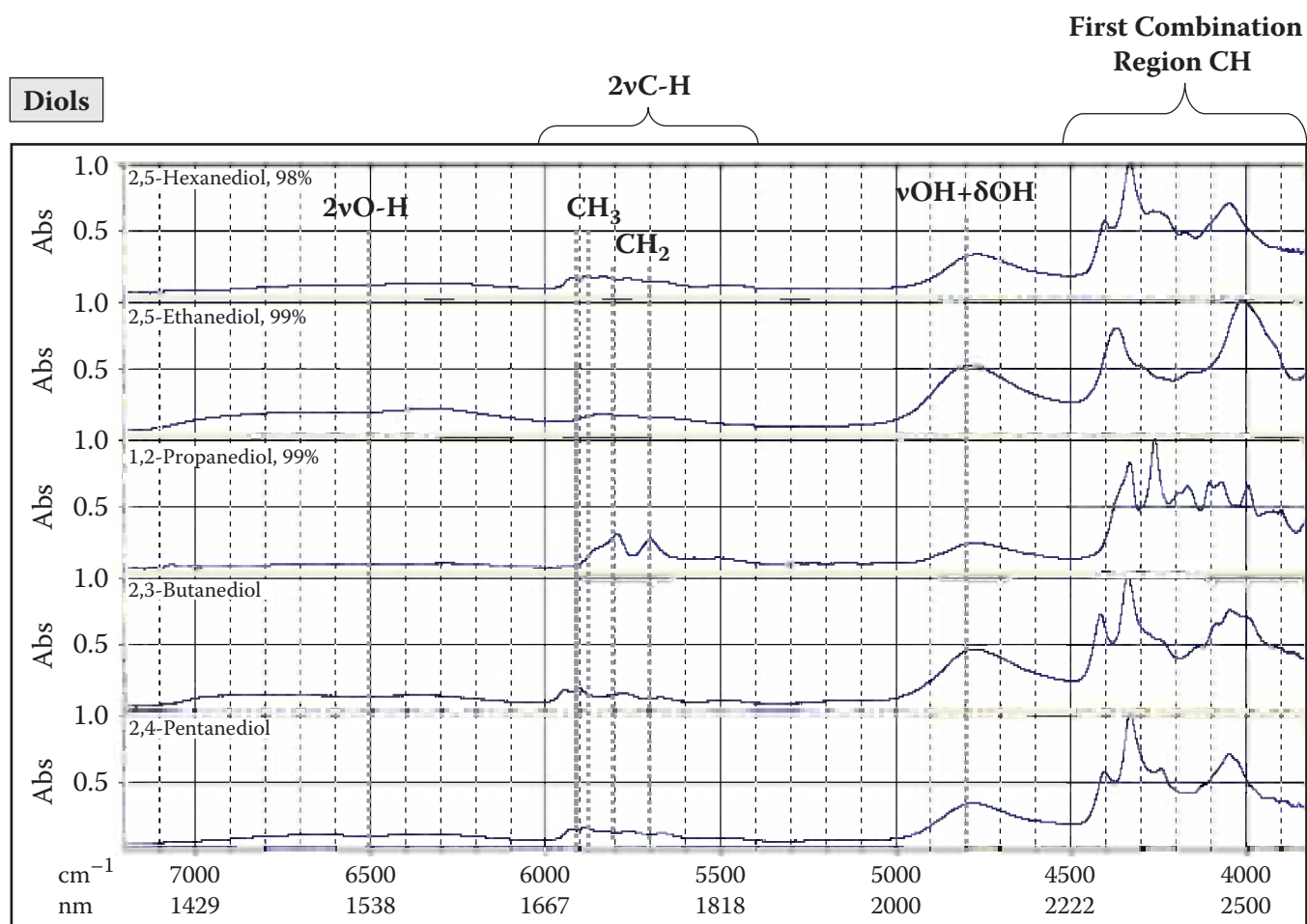
4vC-H



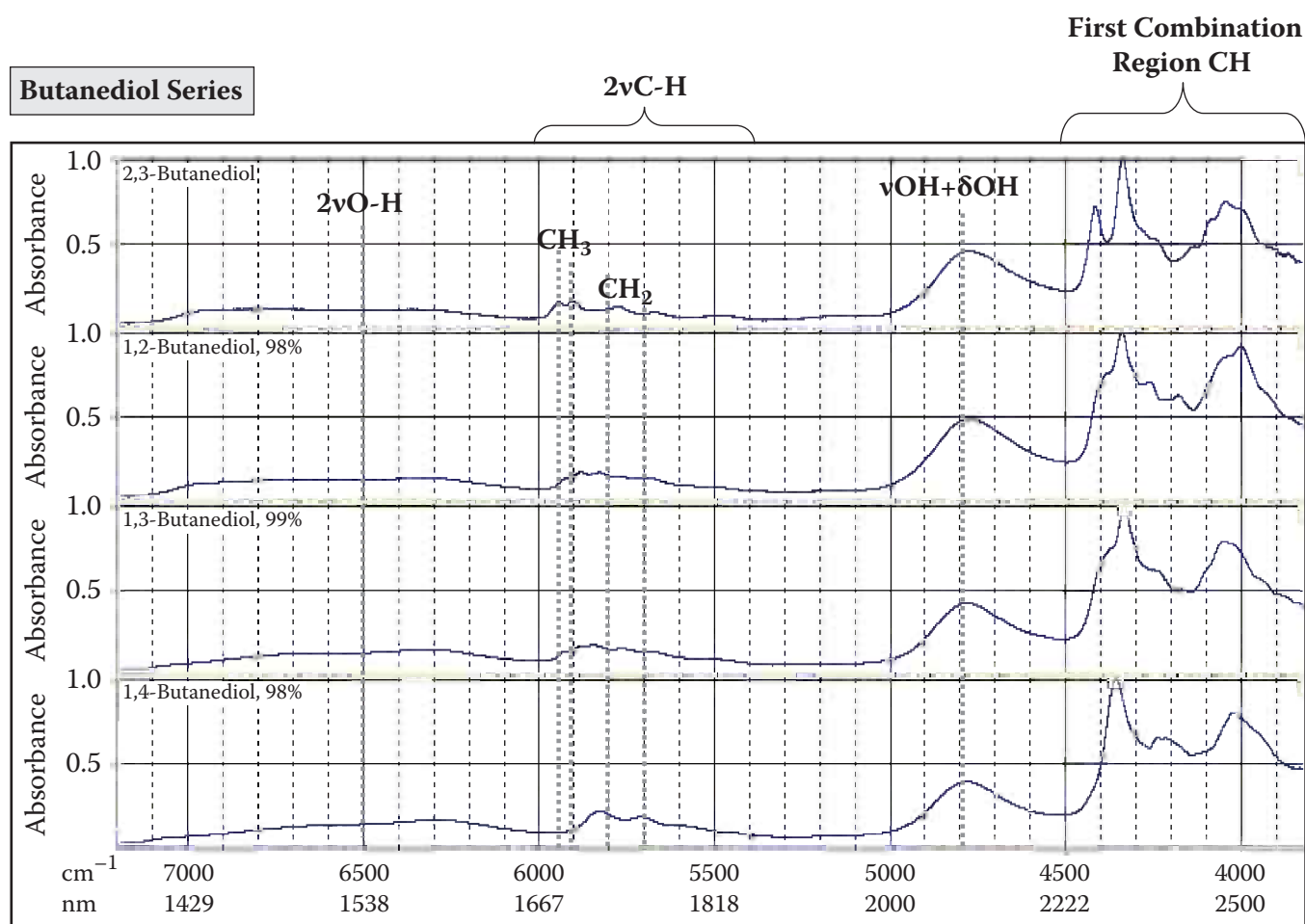
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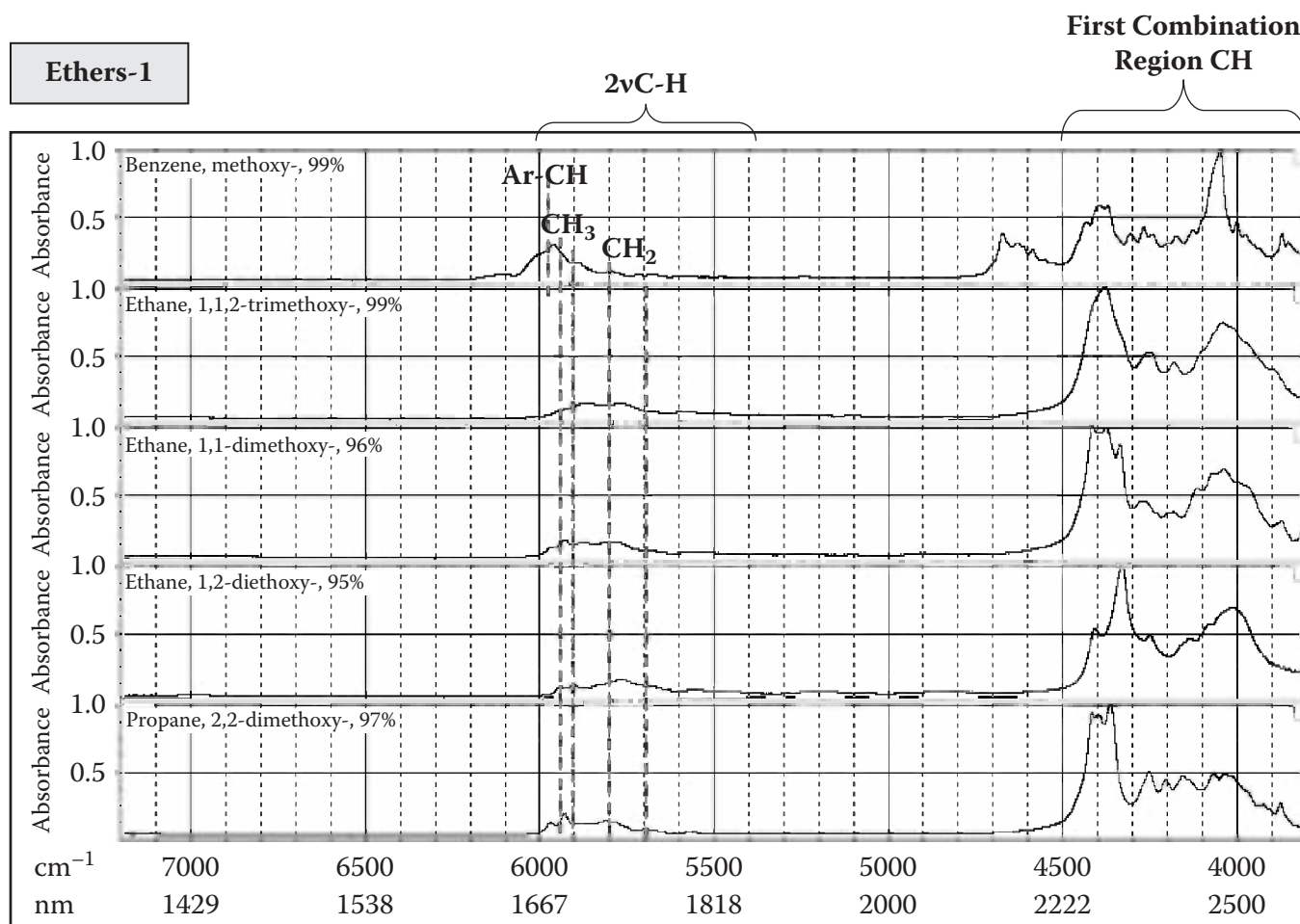


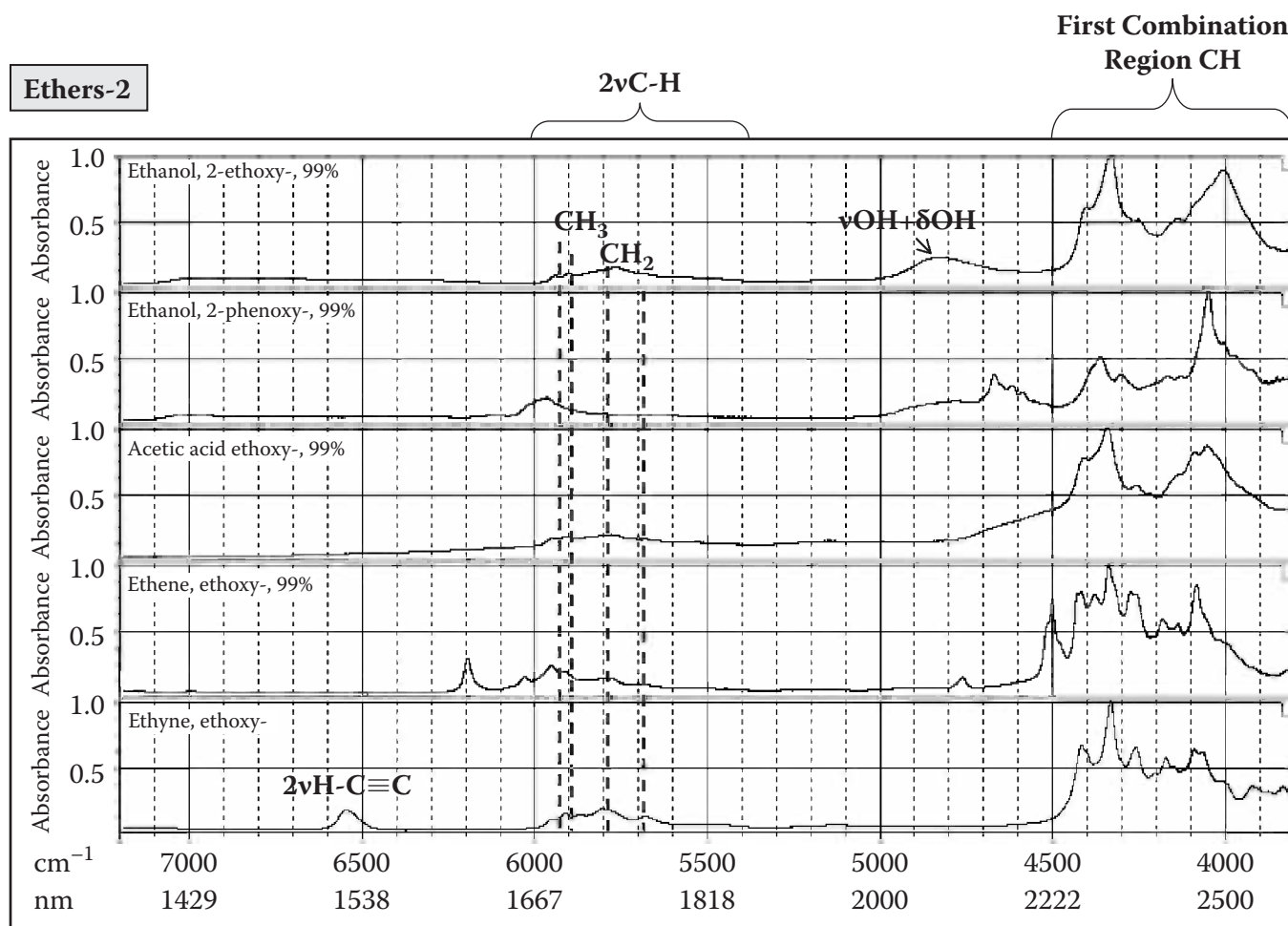


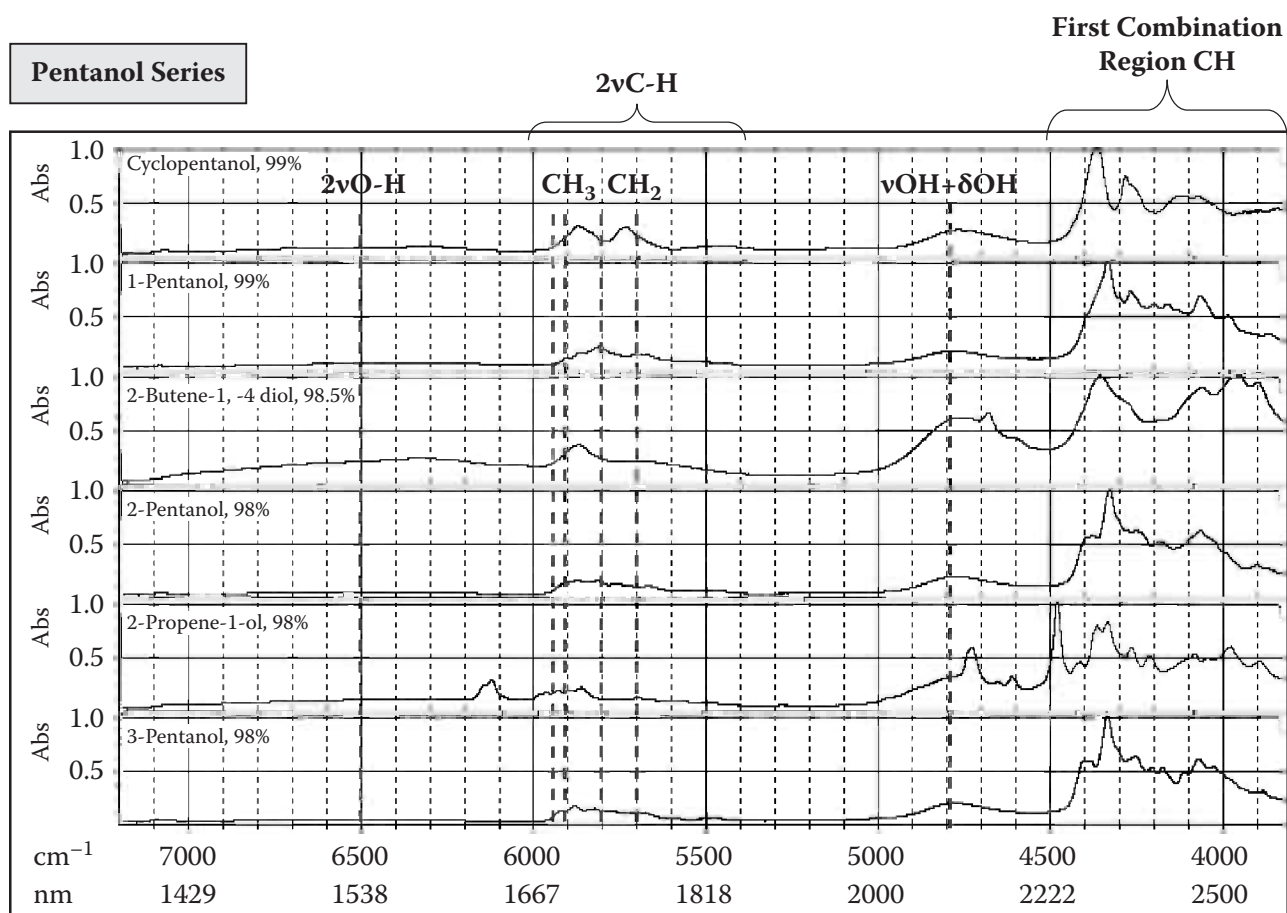


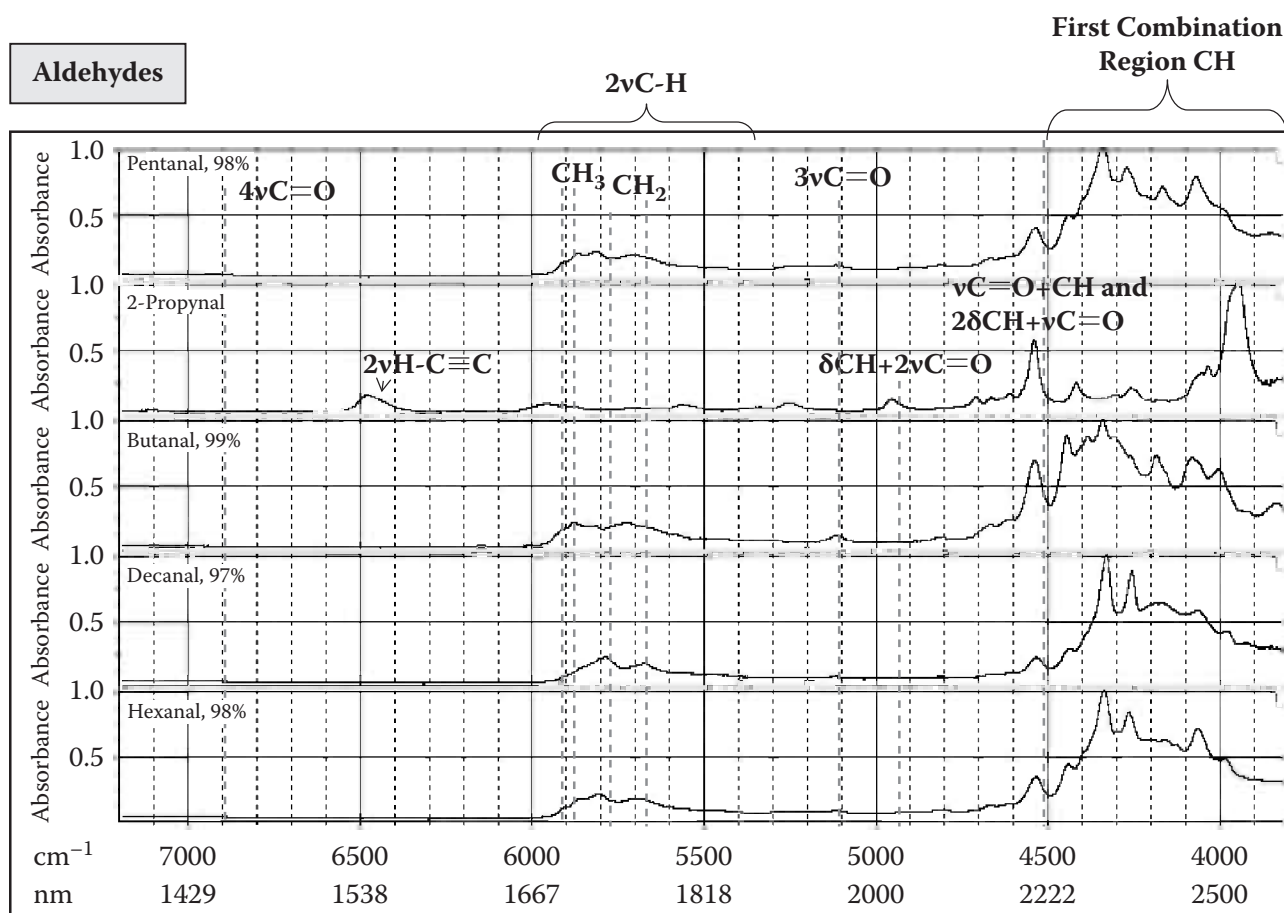


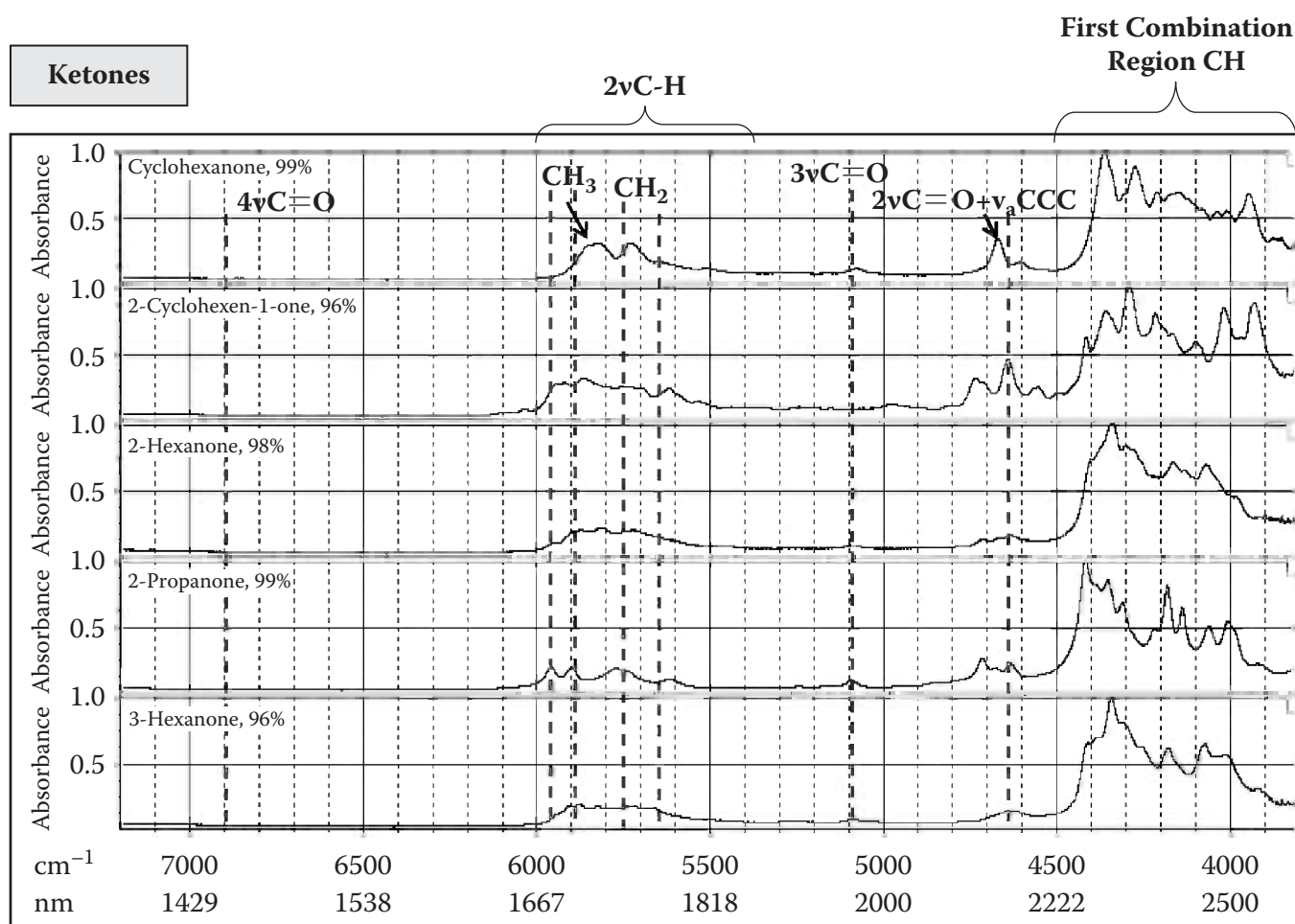


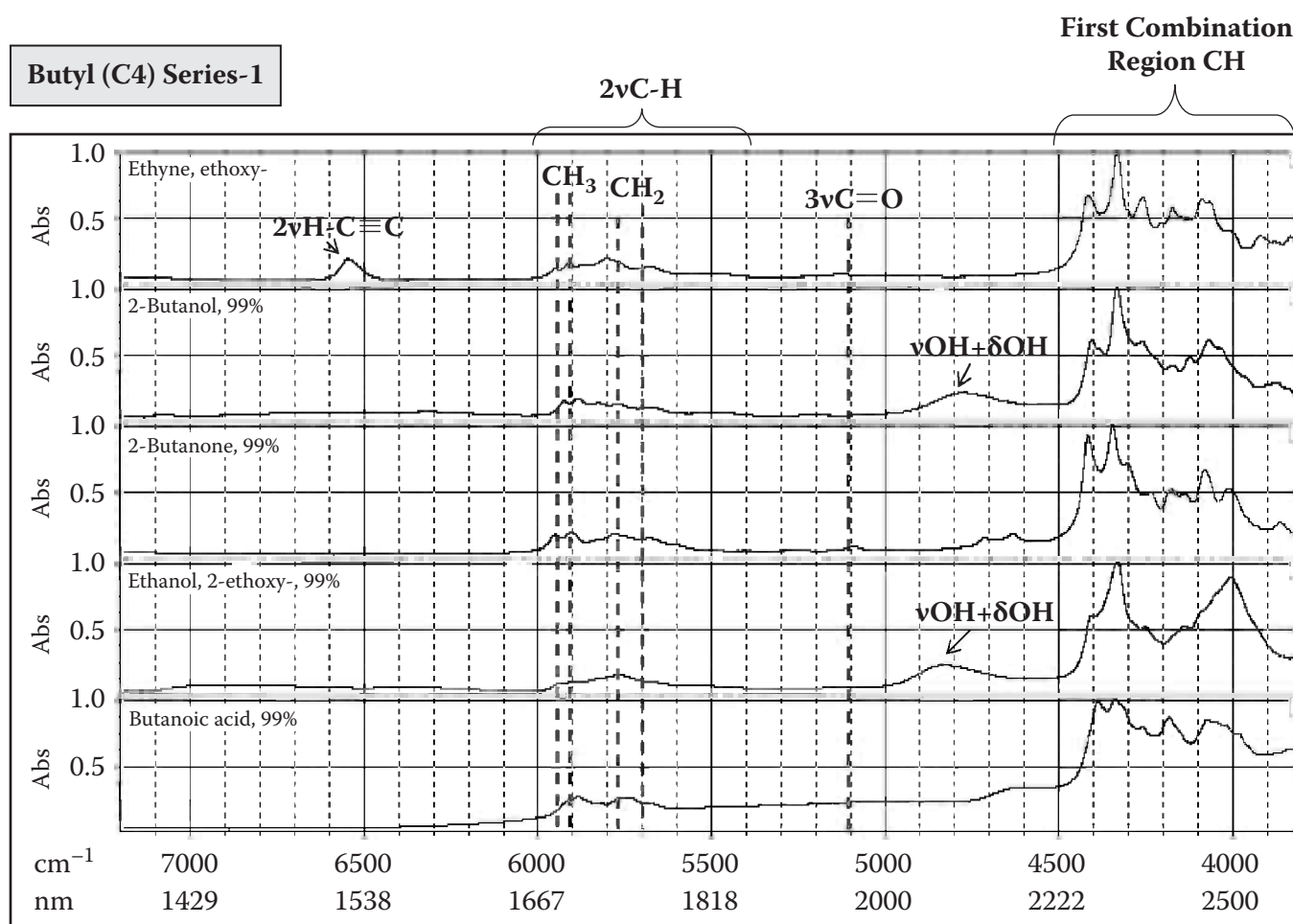


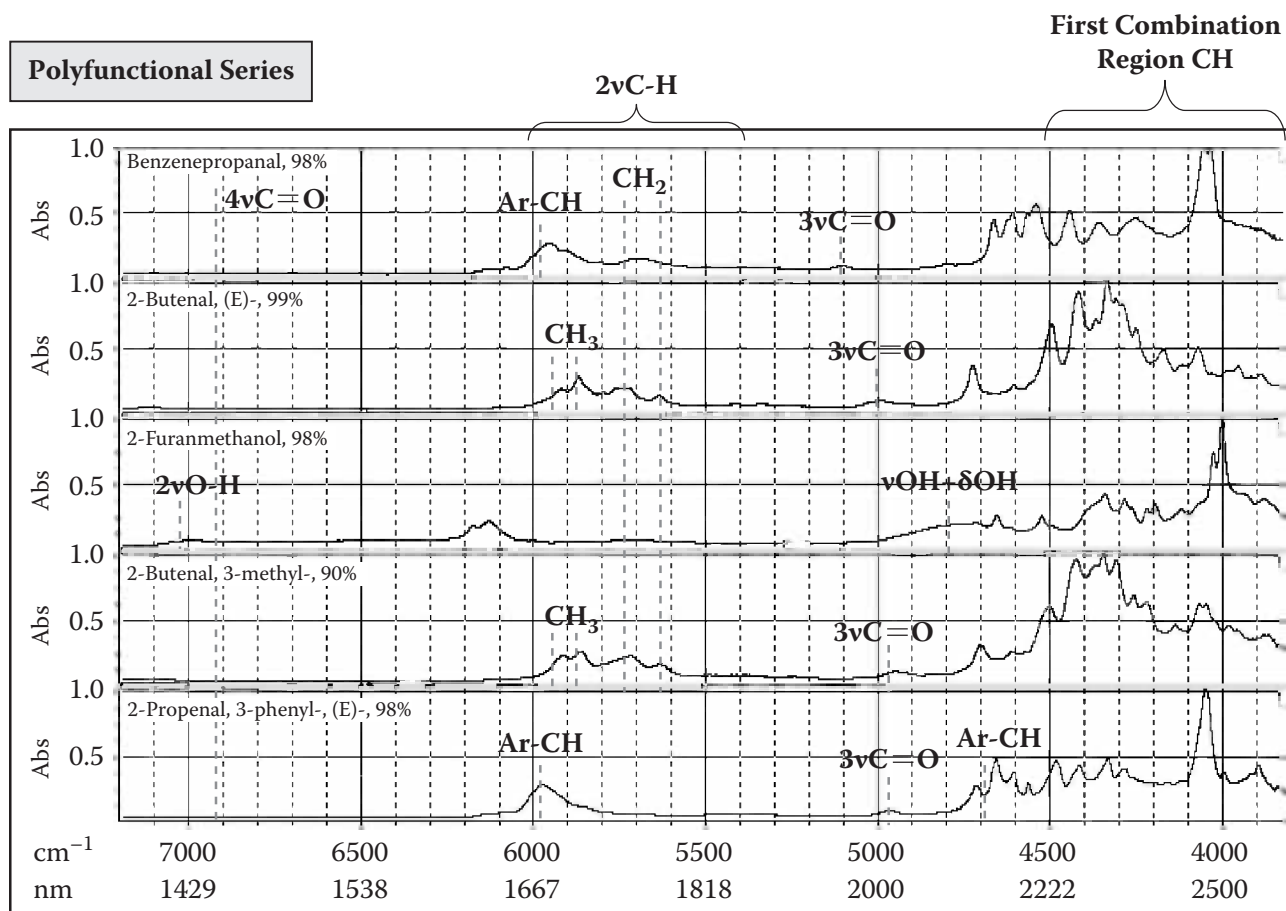




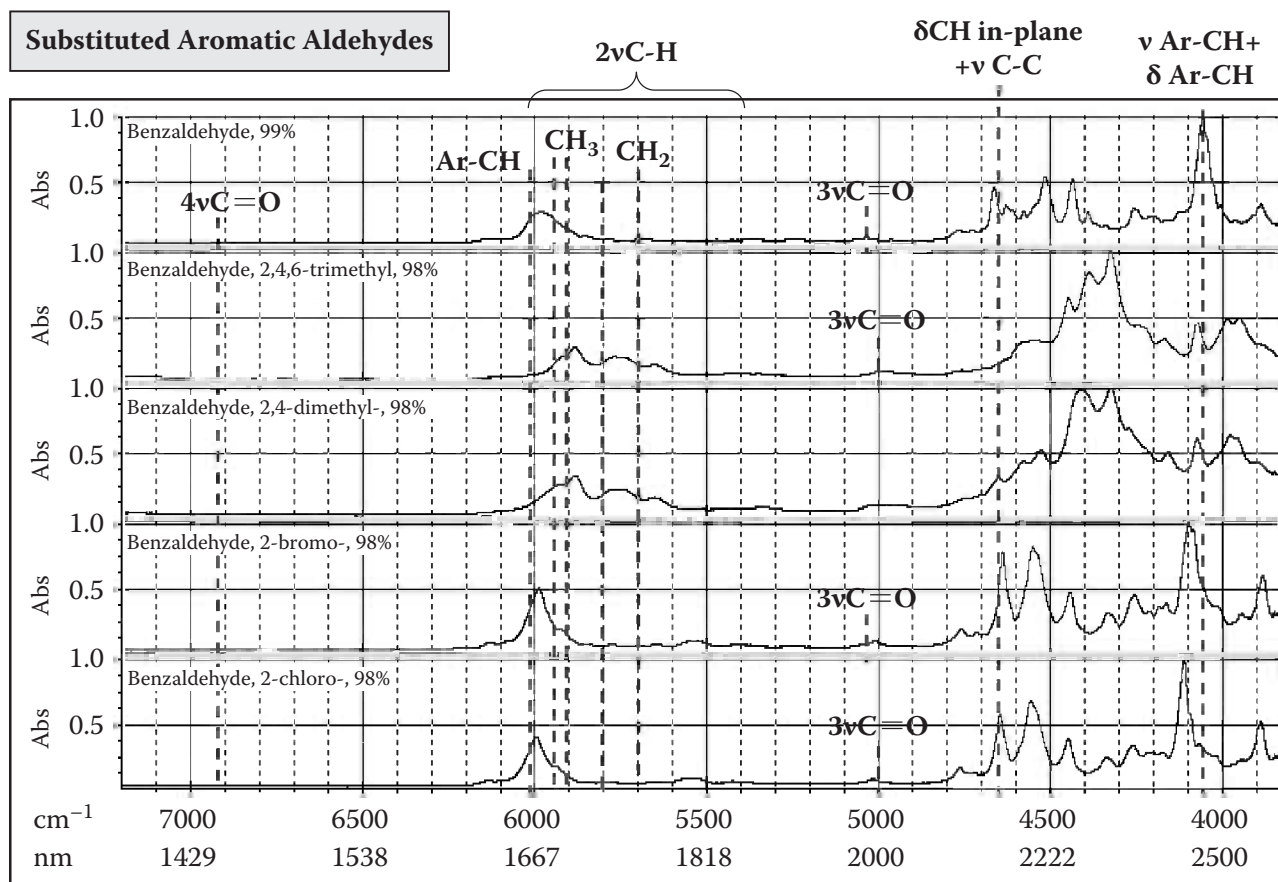


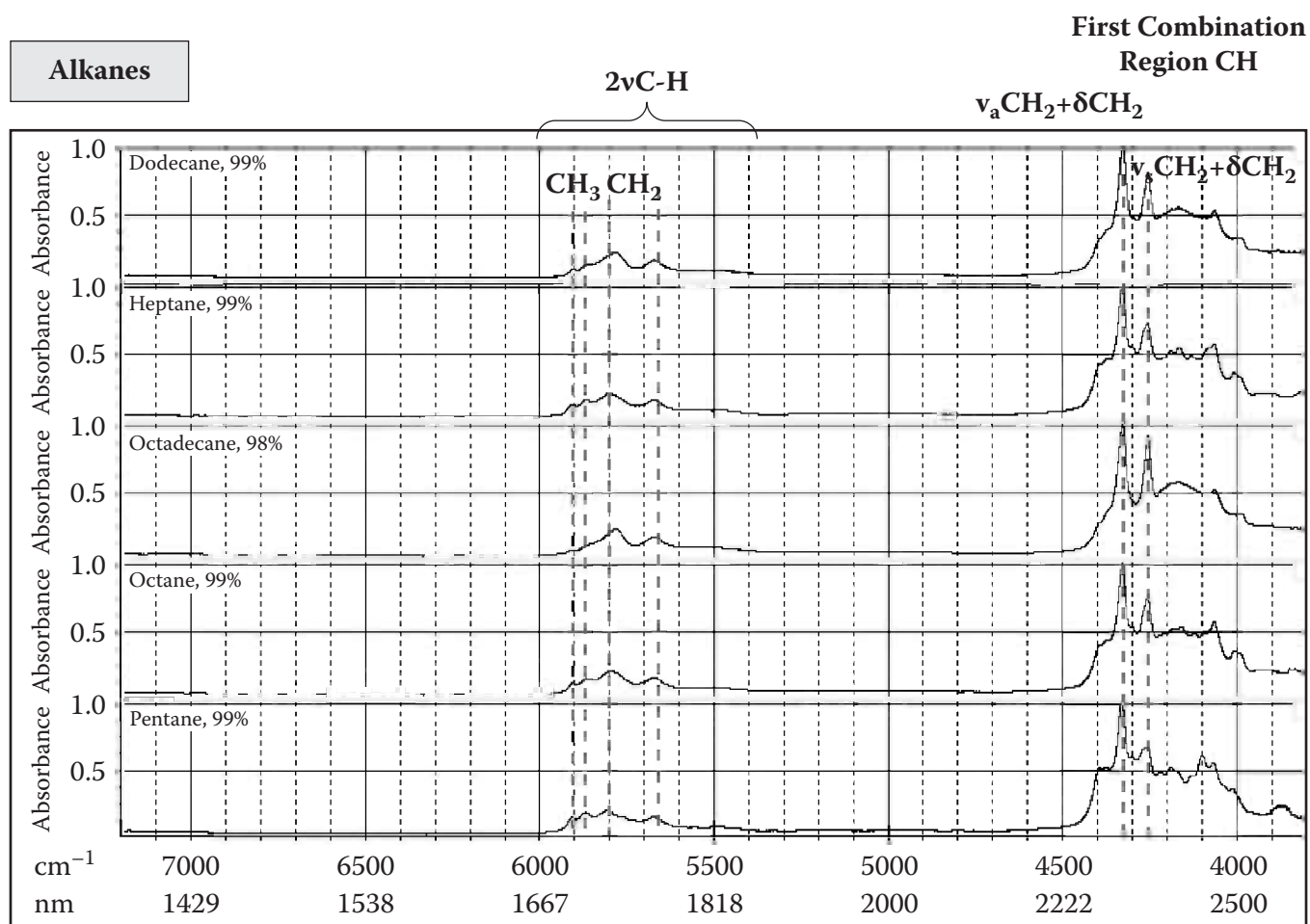


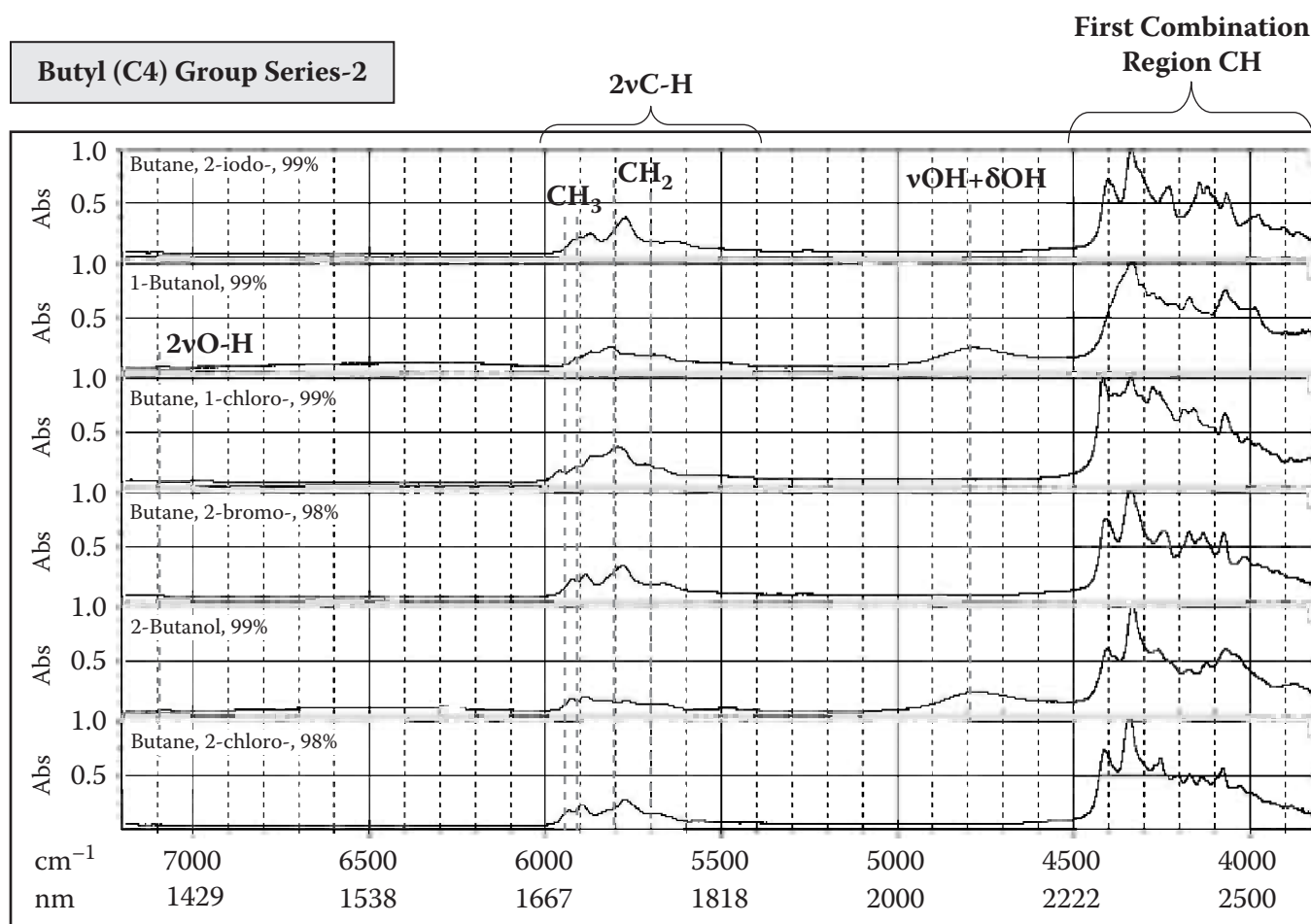


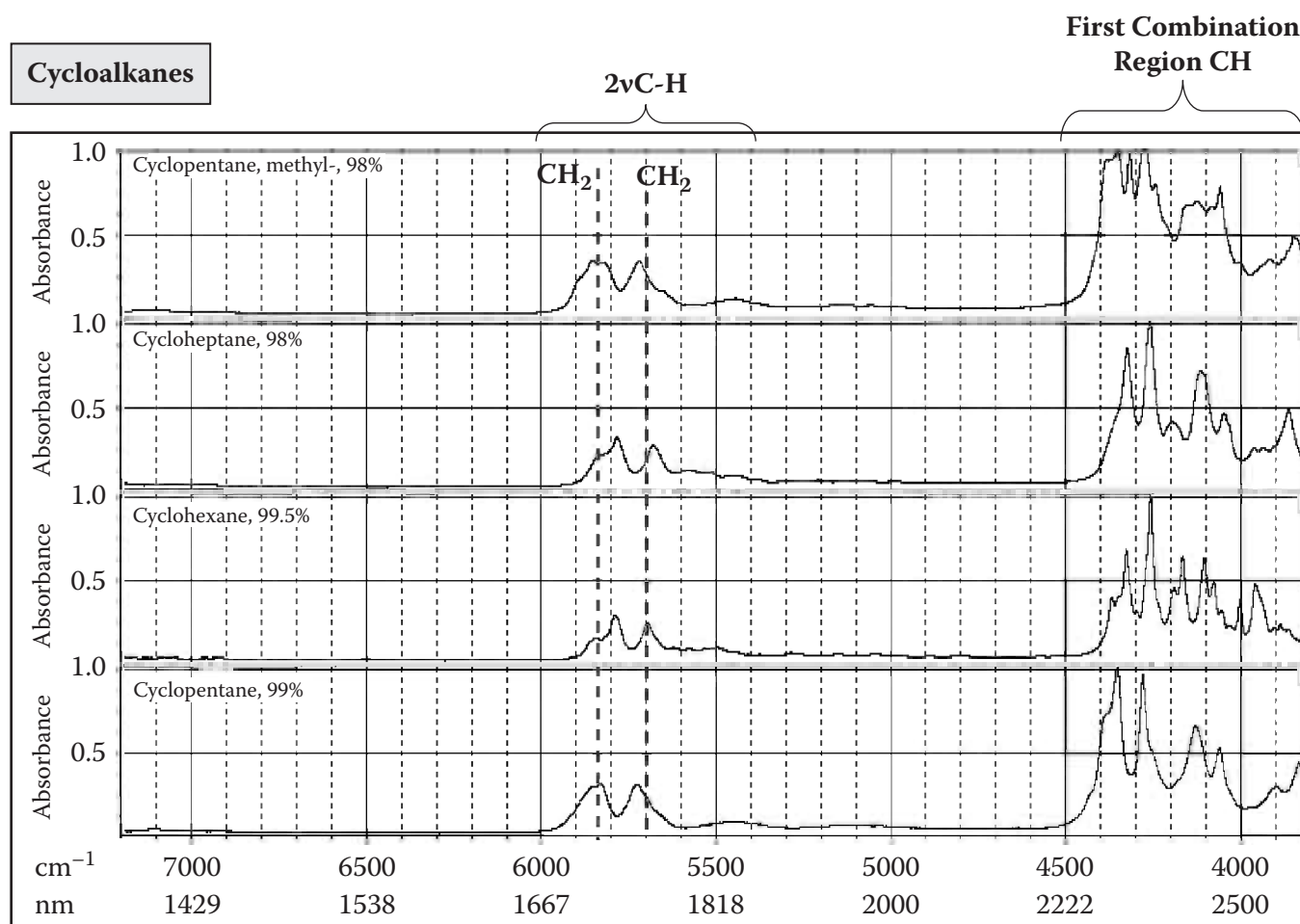


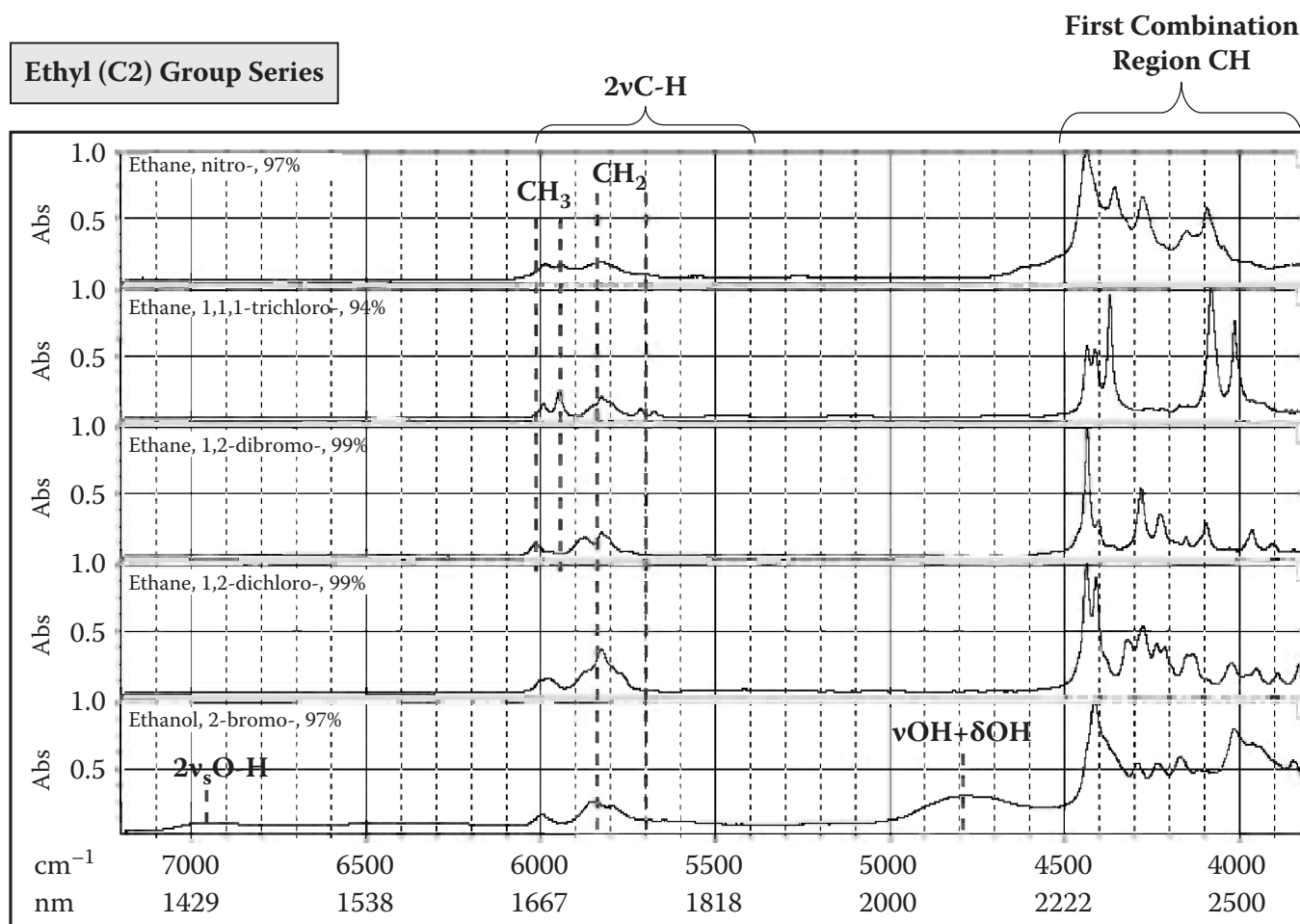


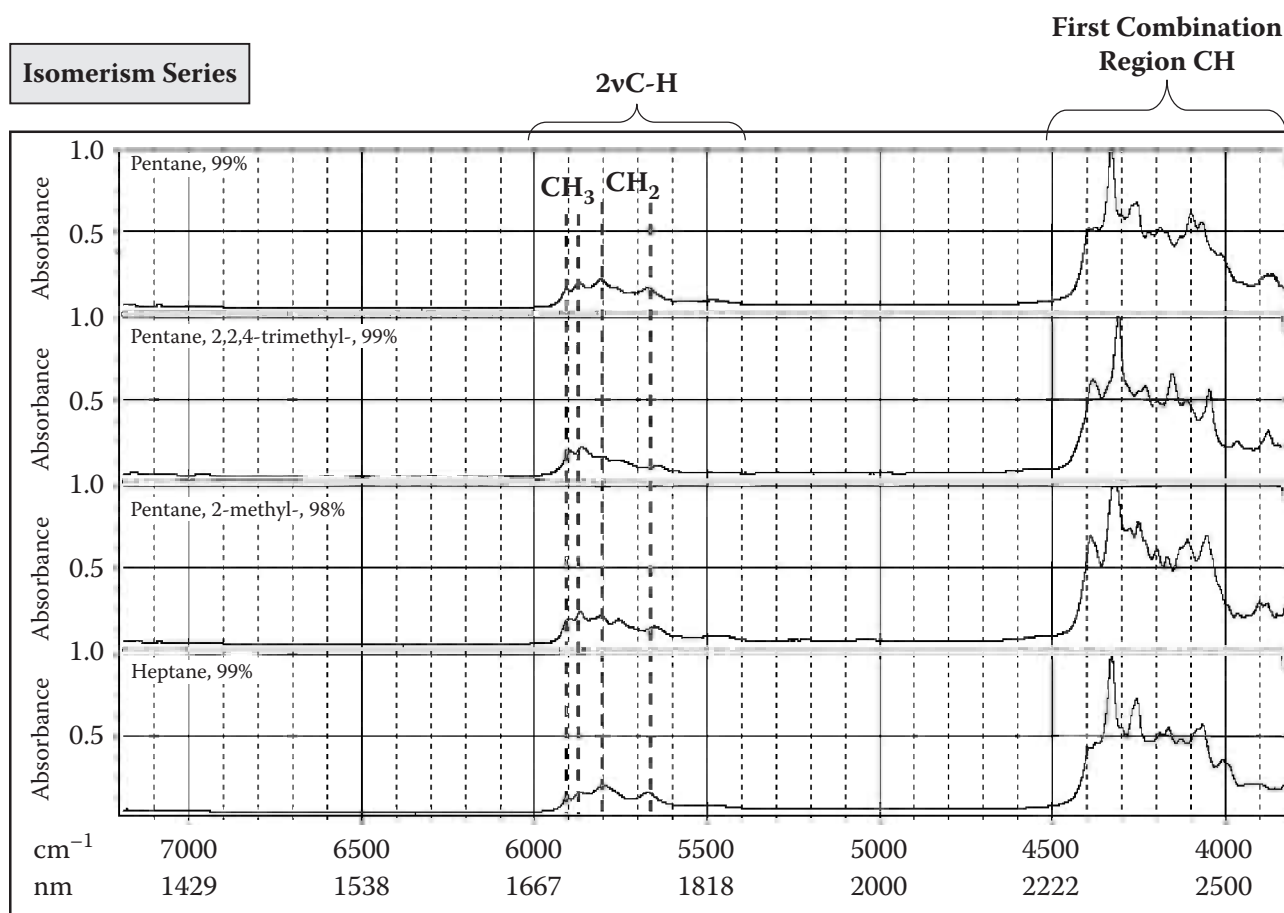


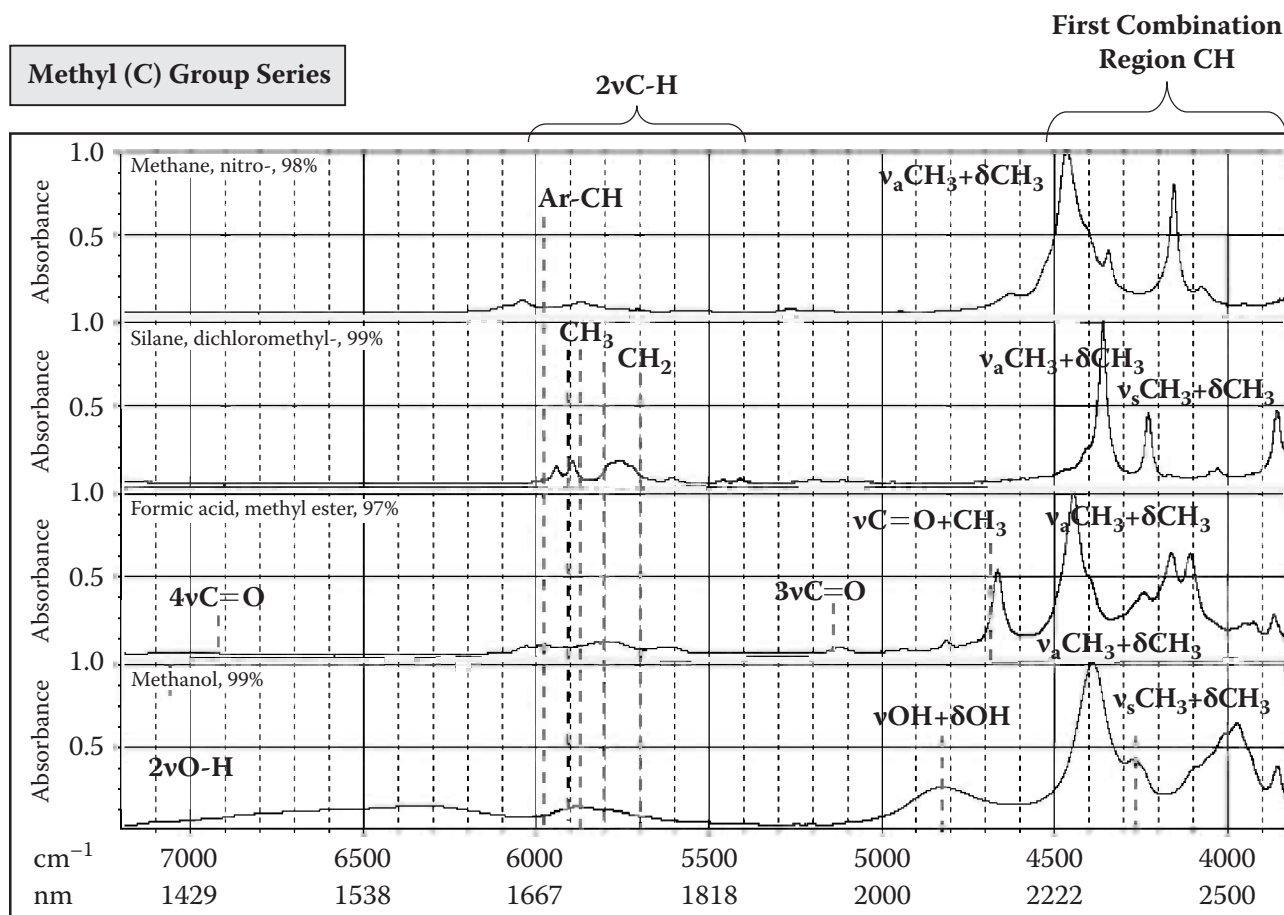


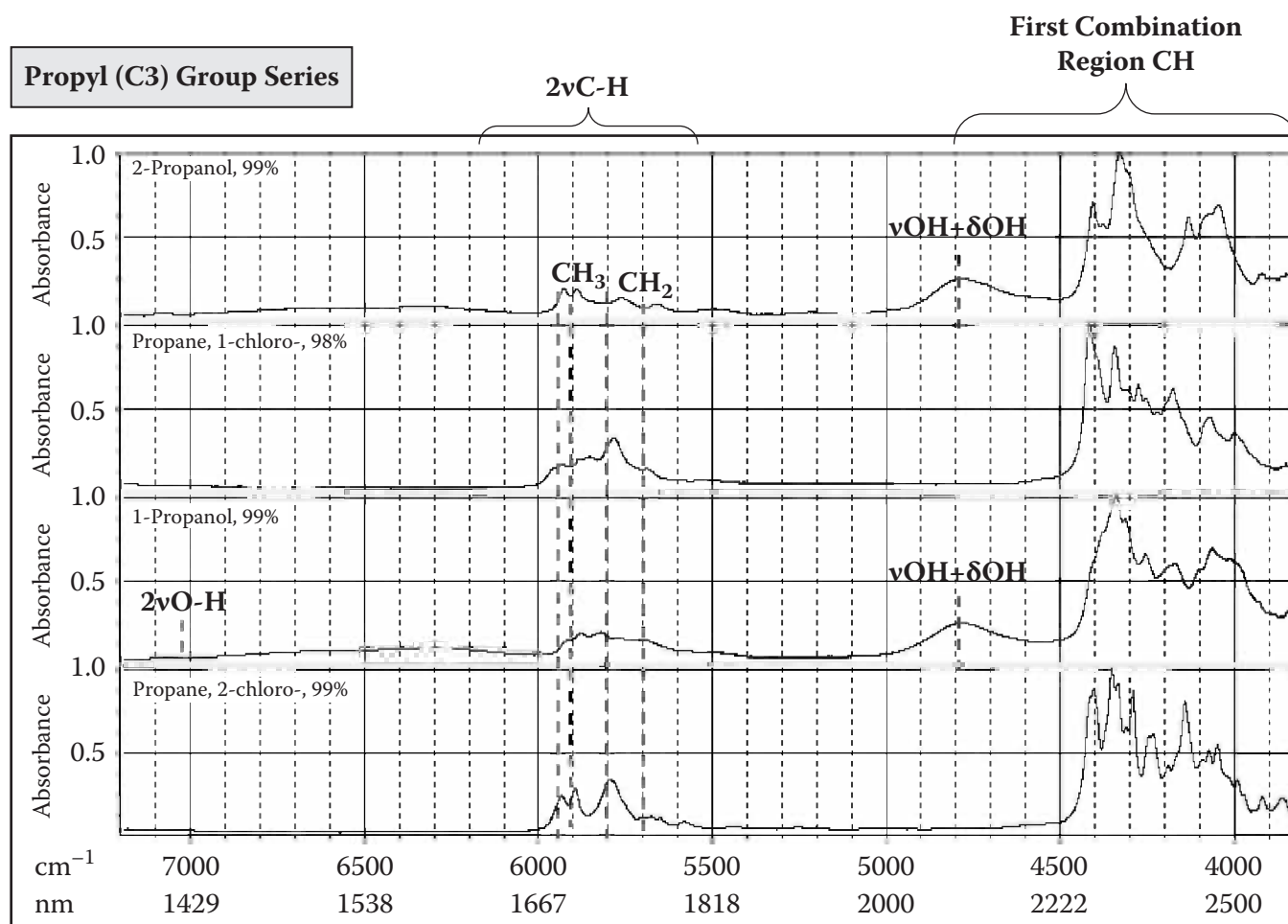




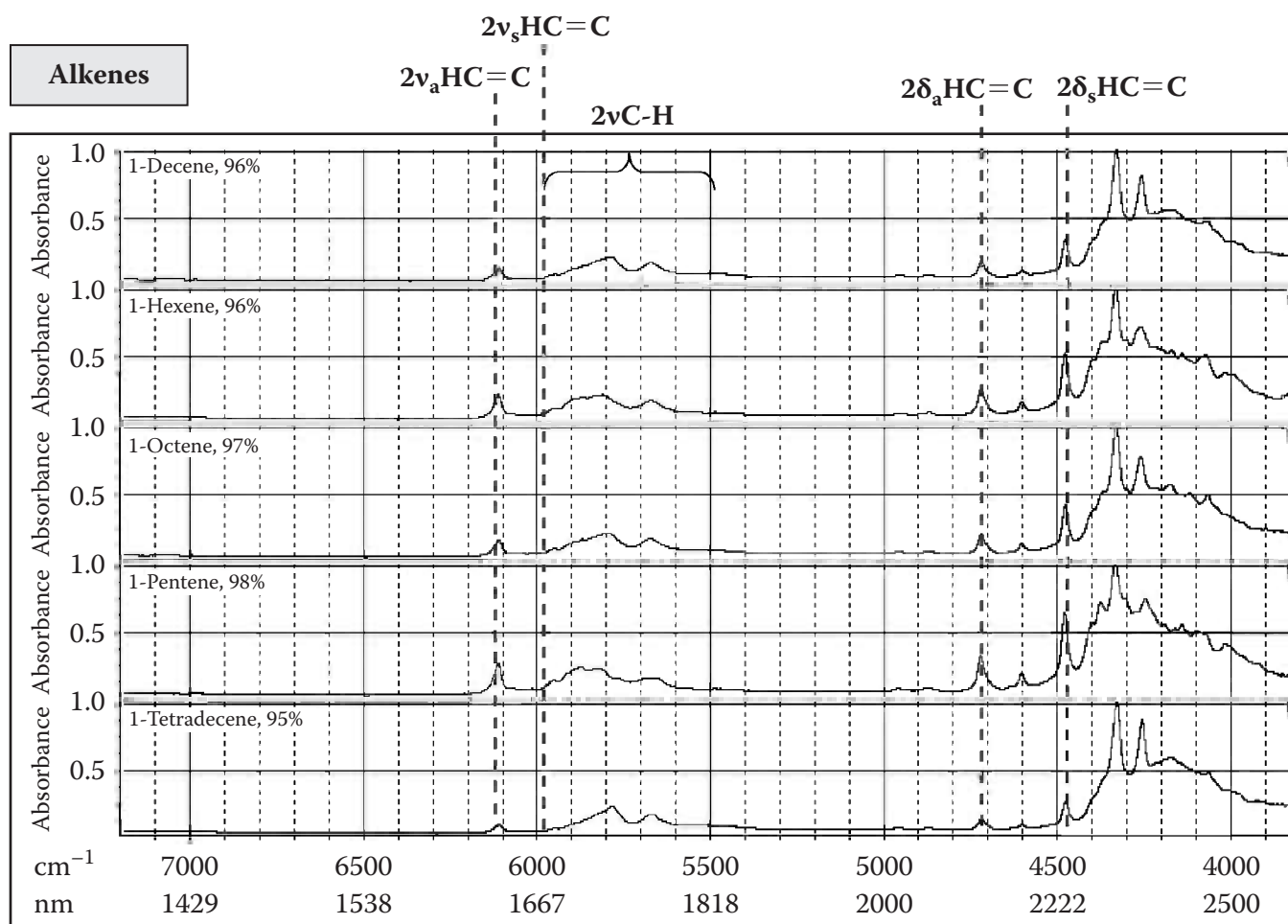


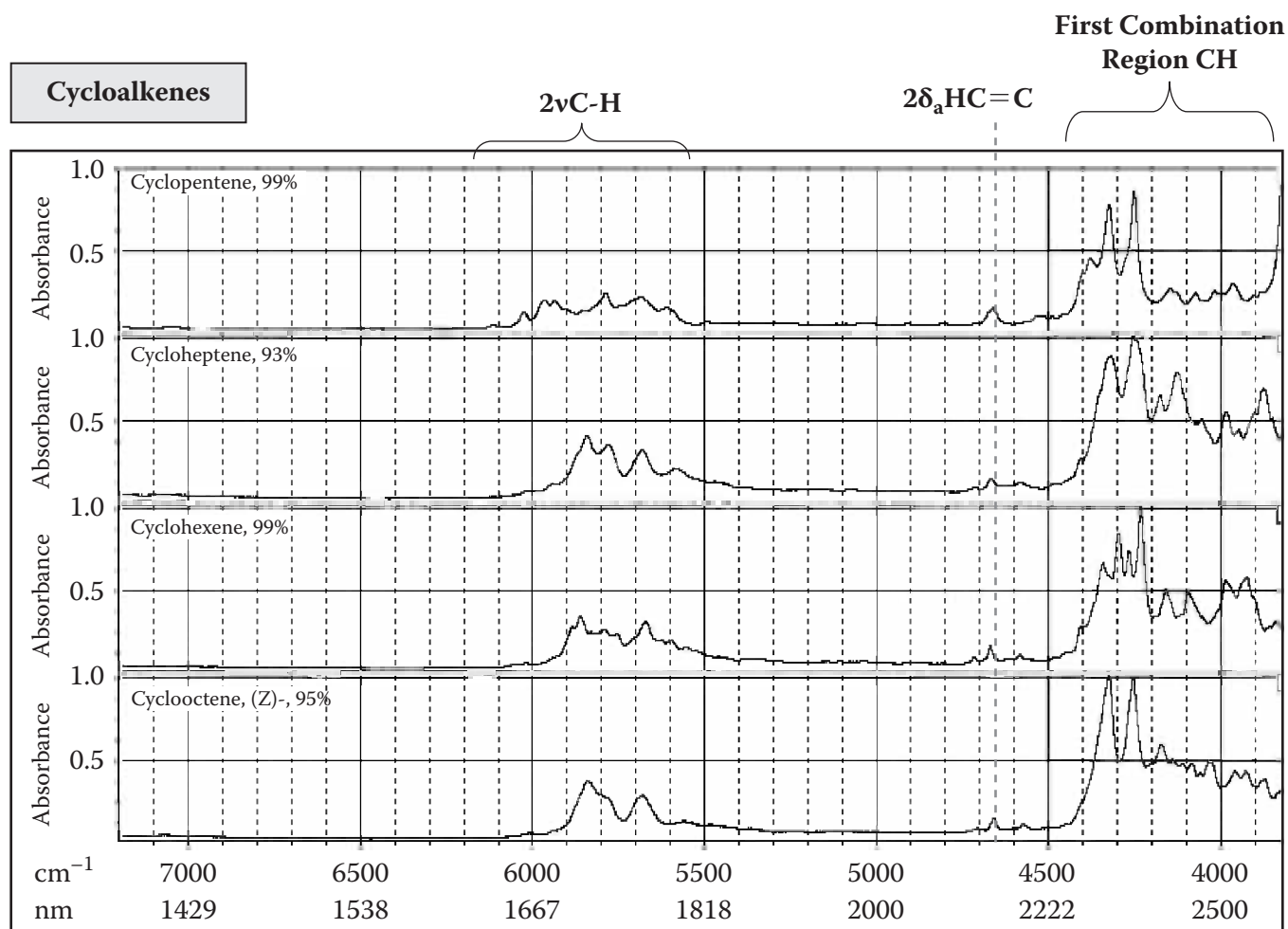


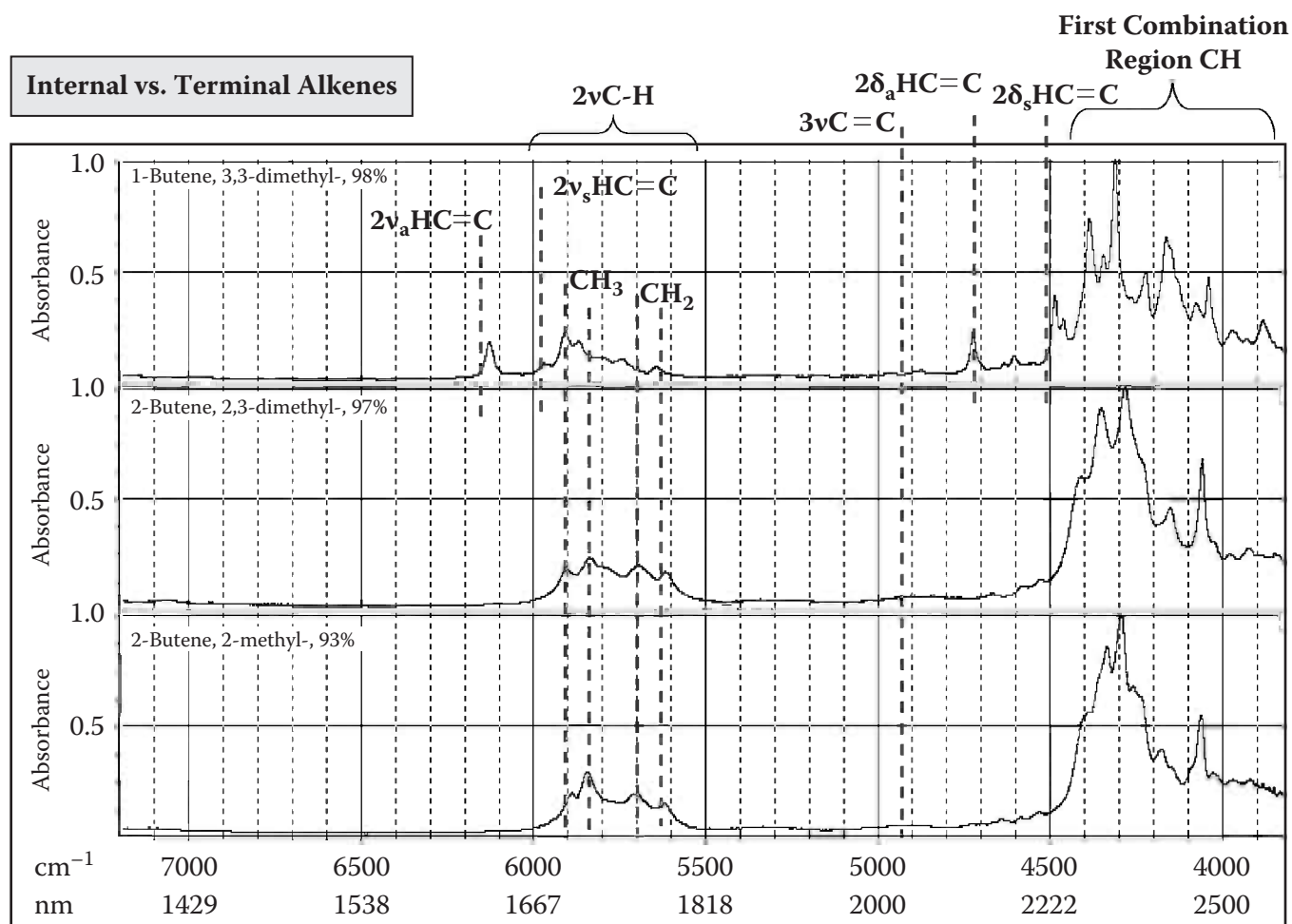


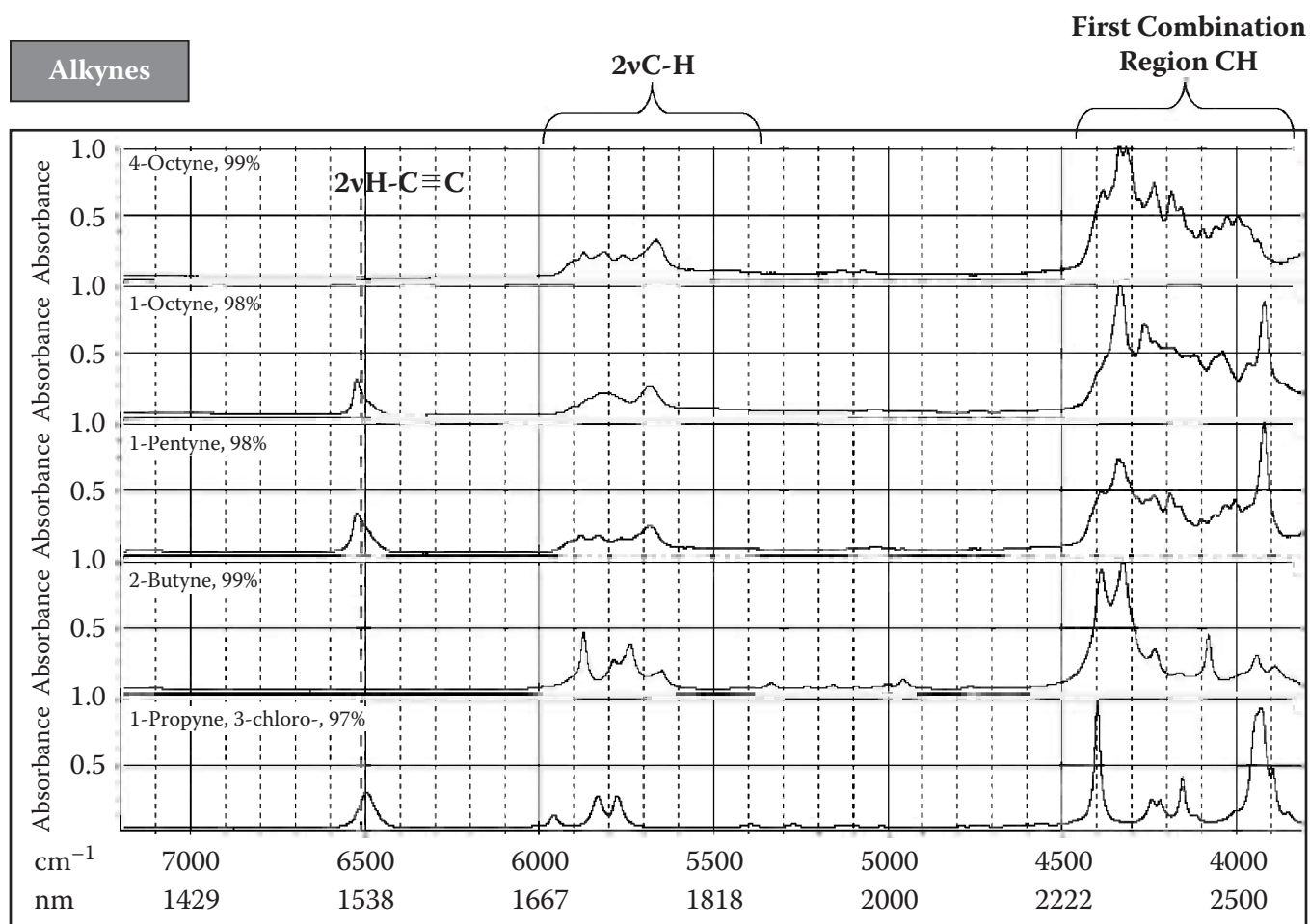


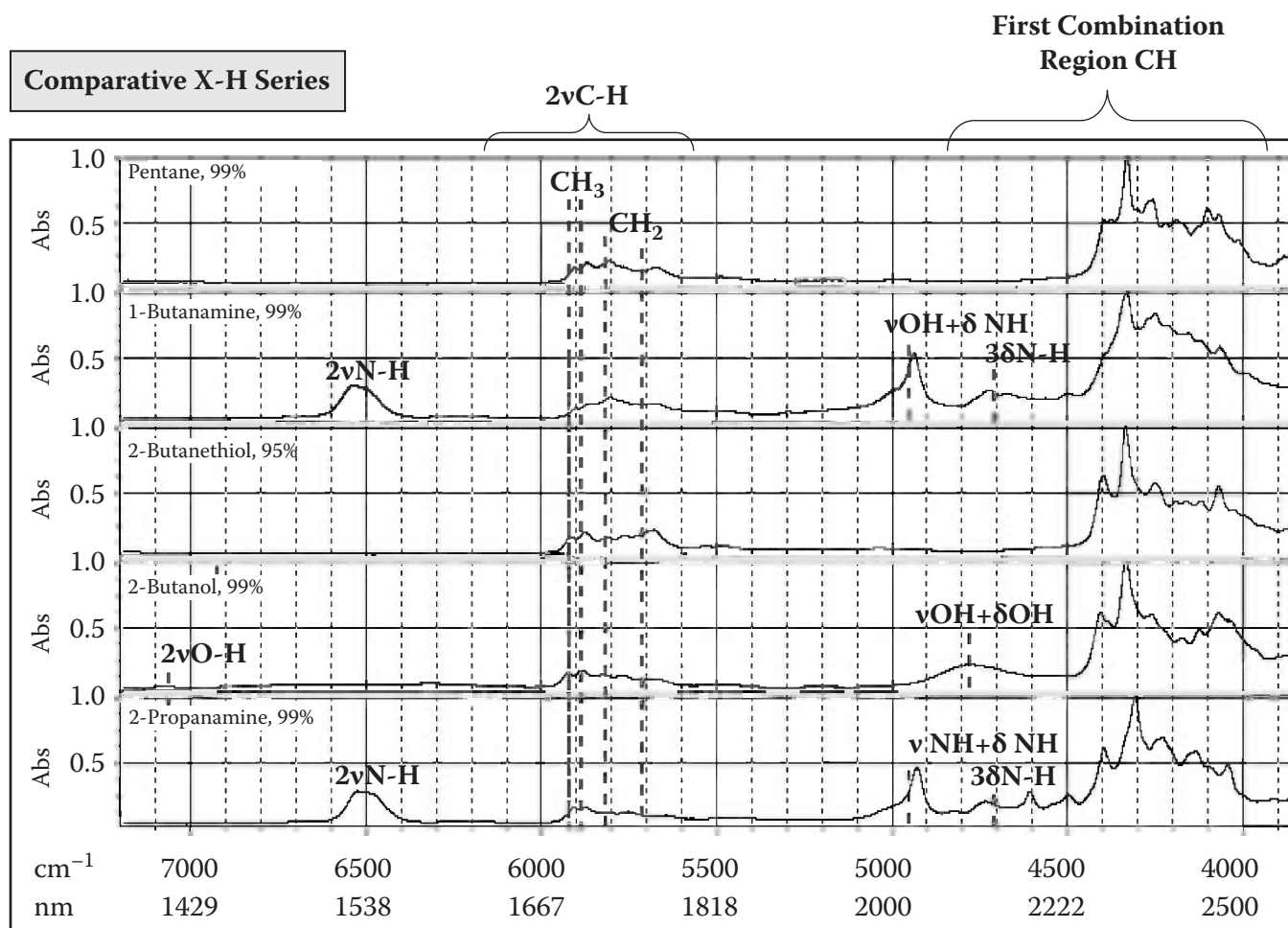


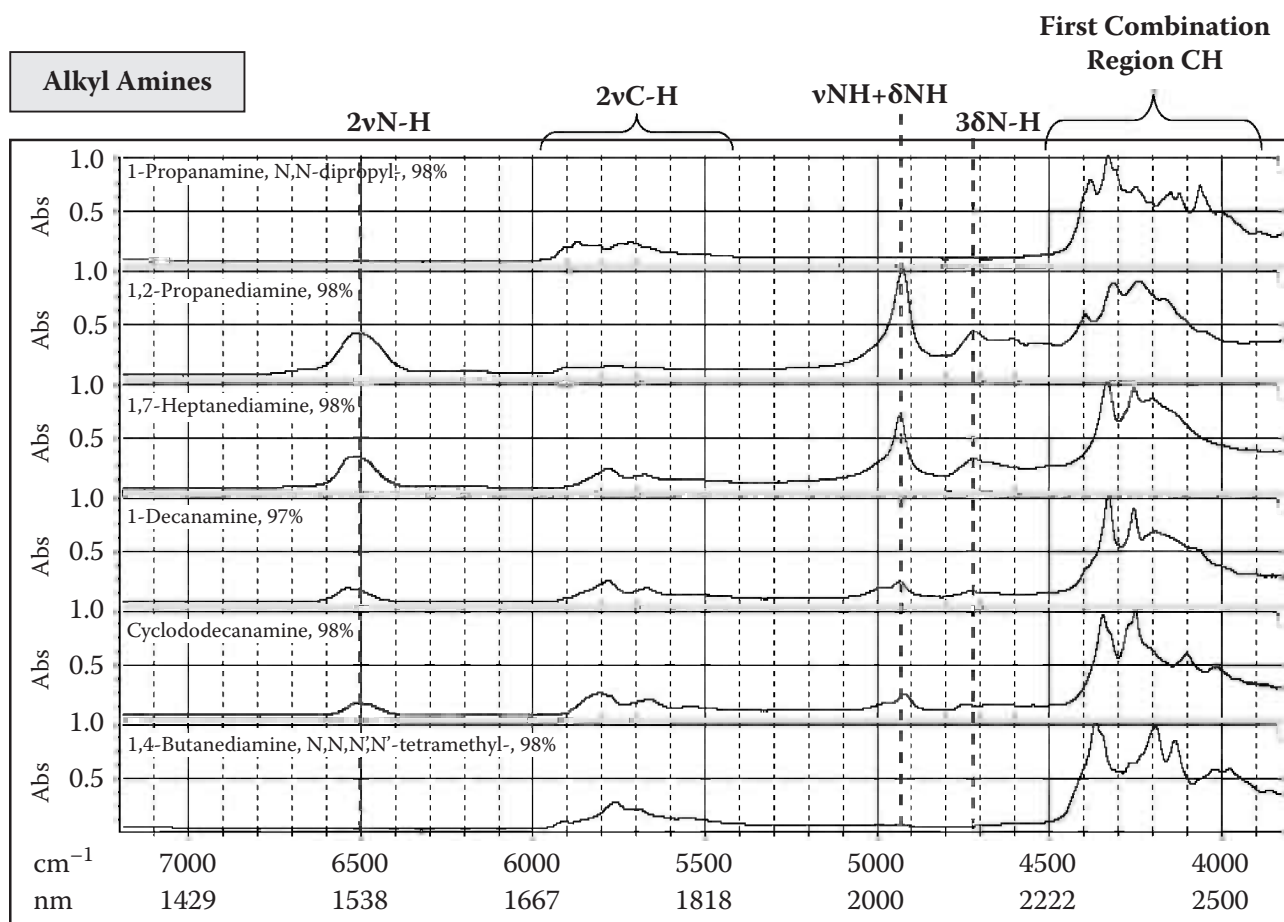


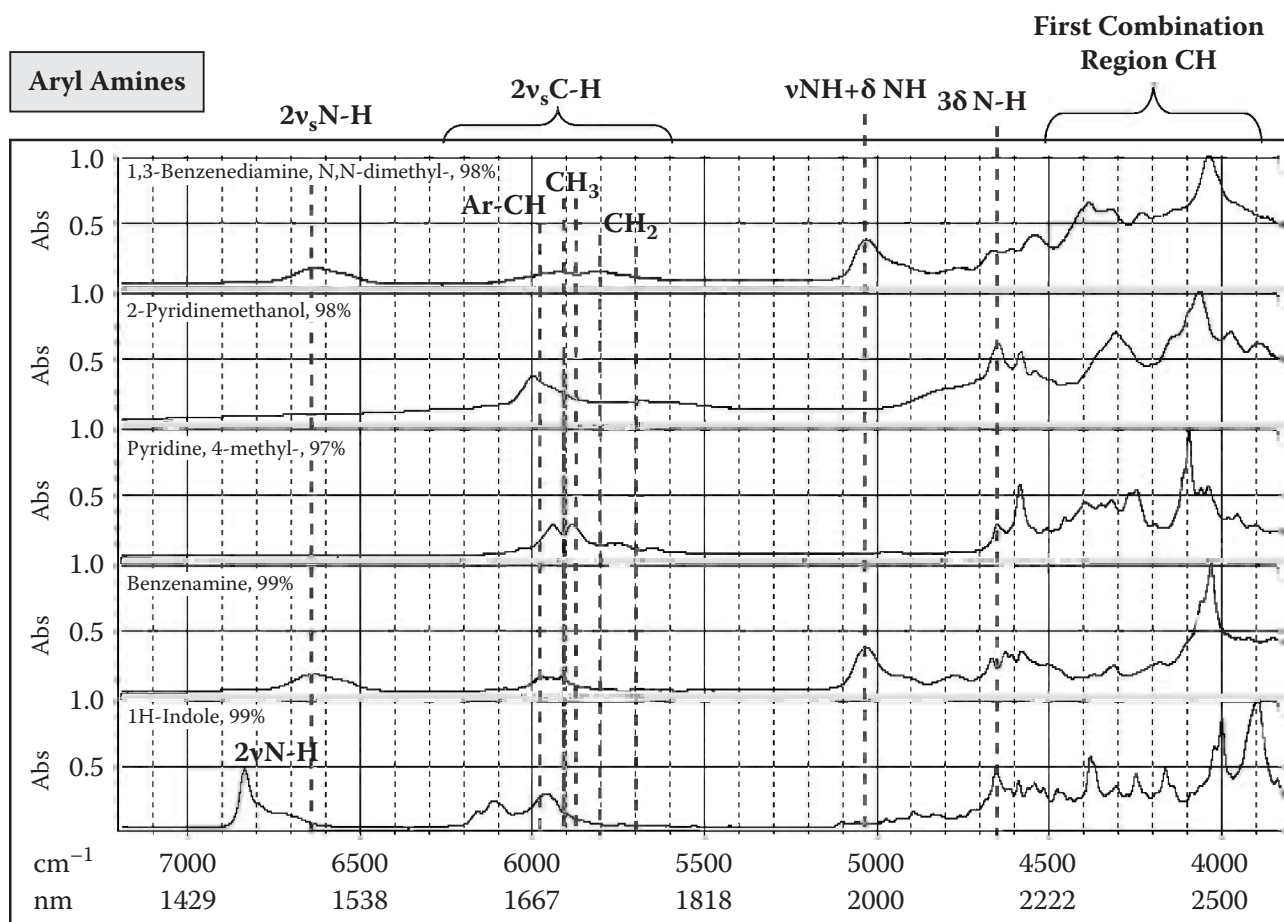


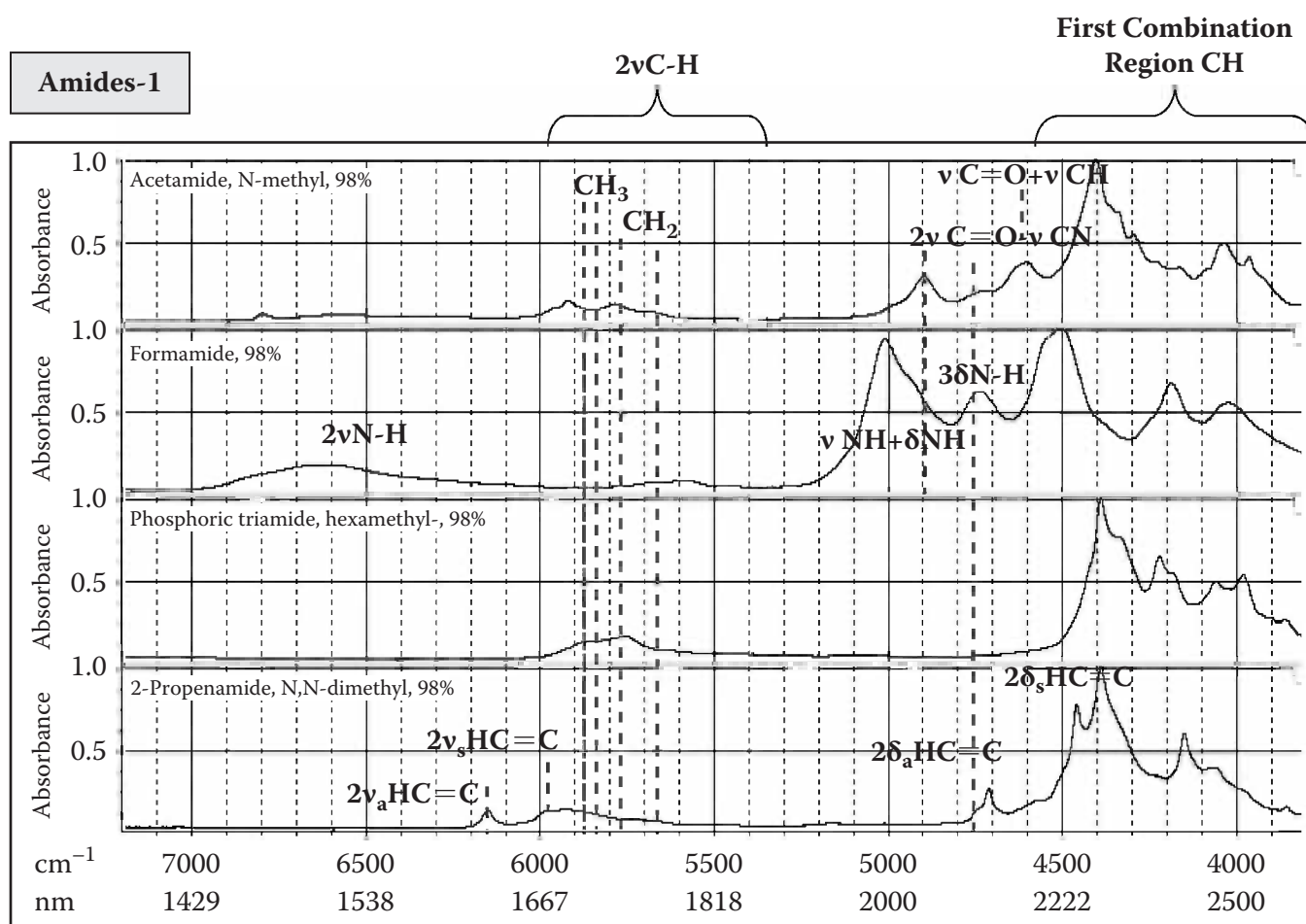




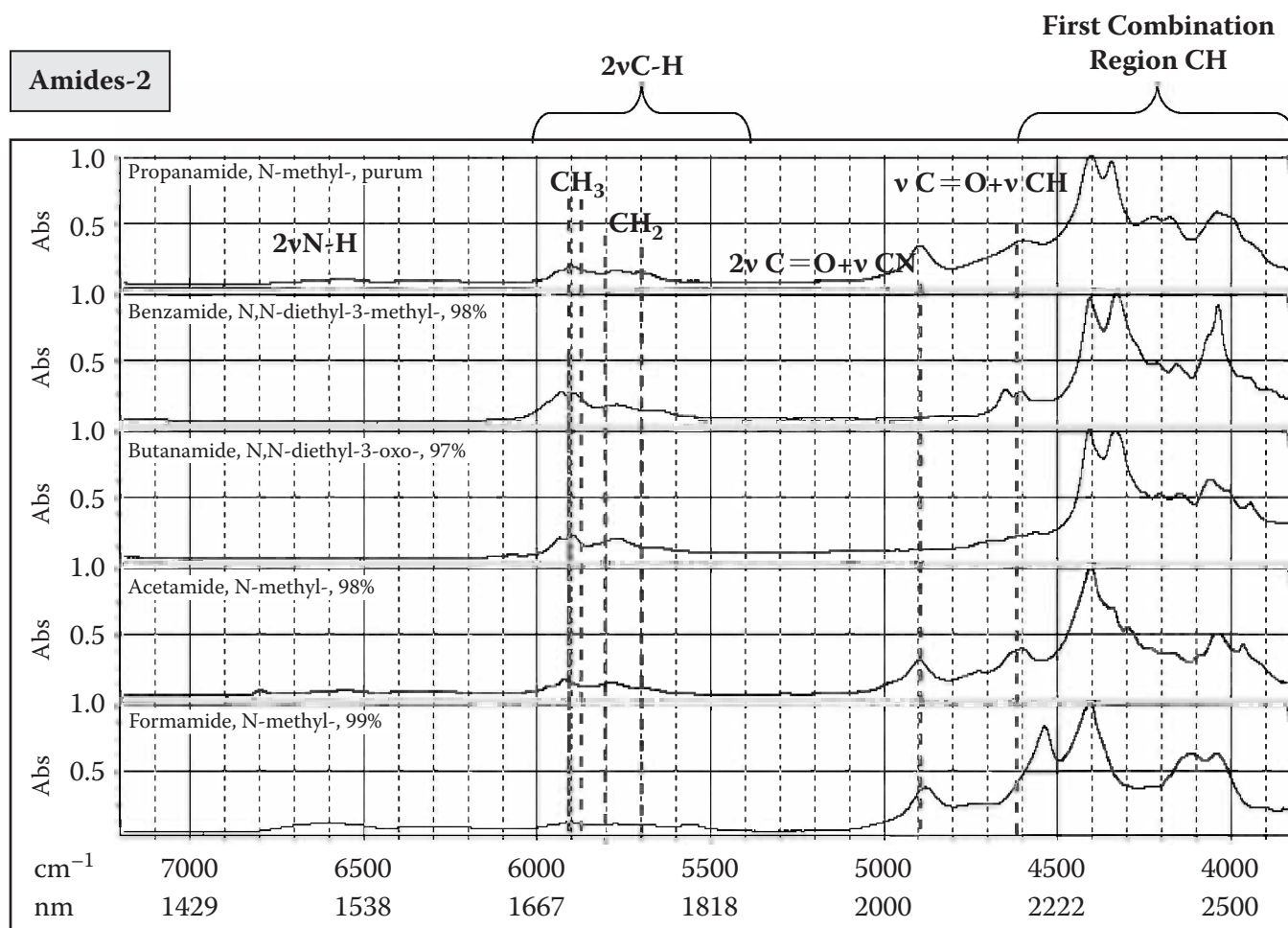


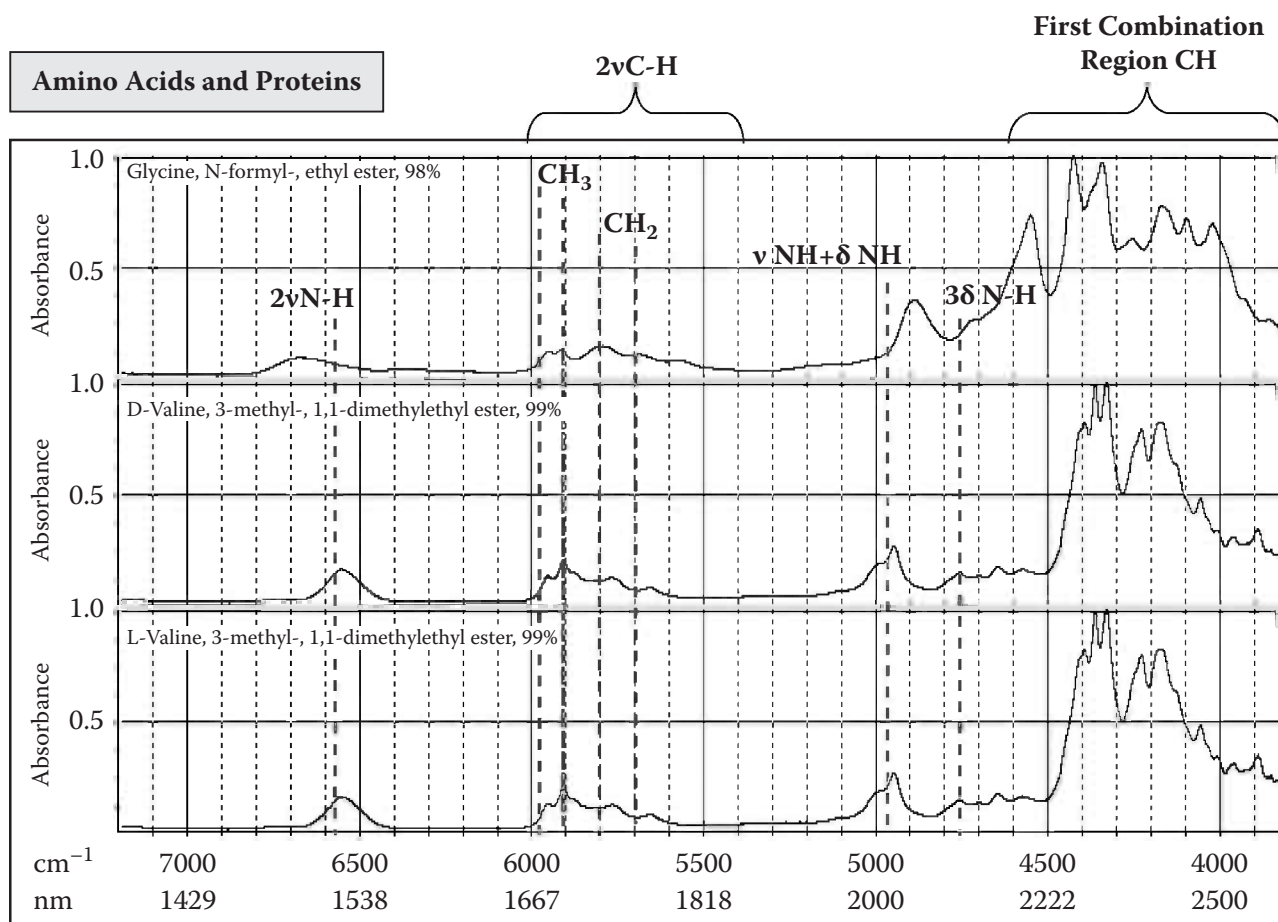


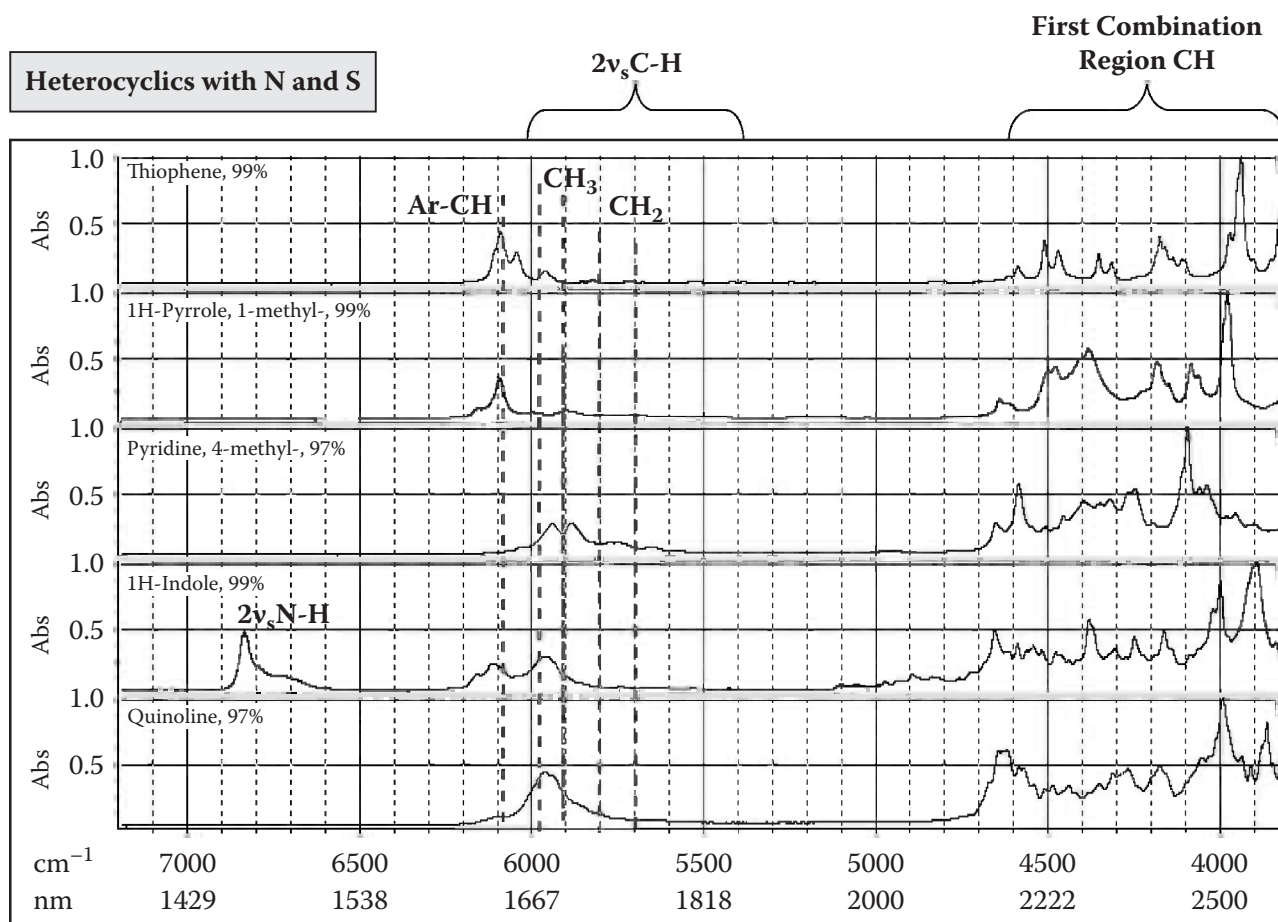


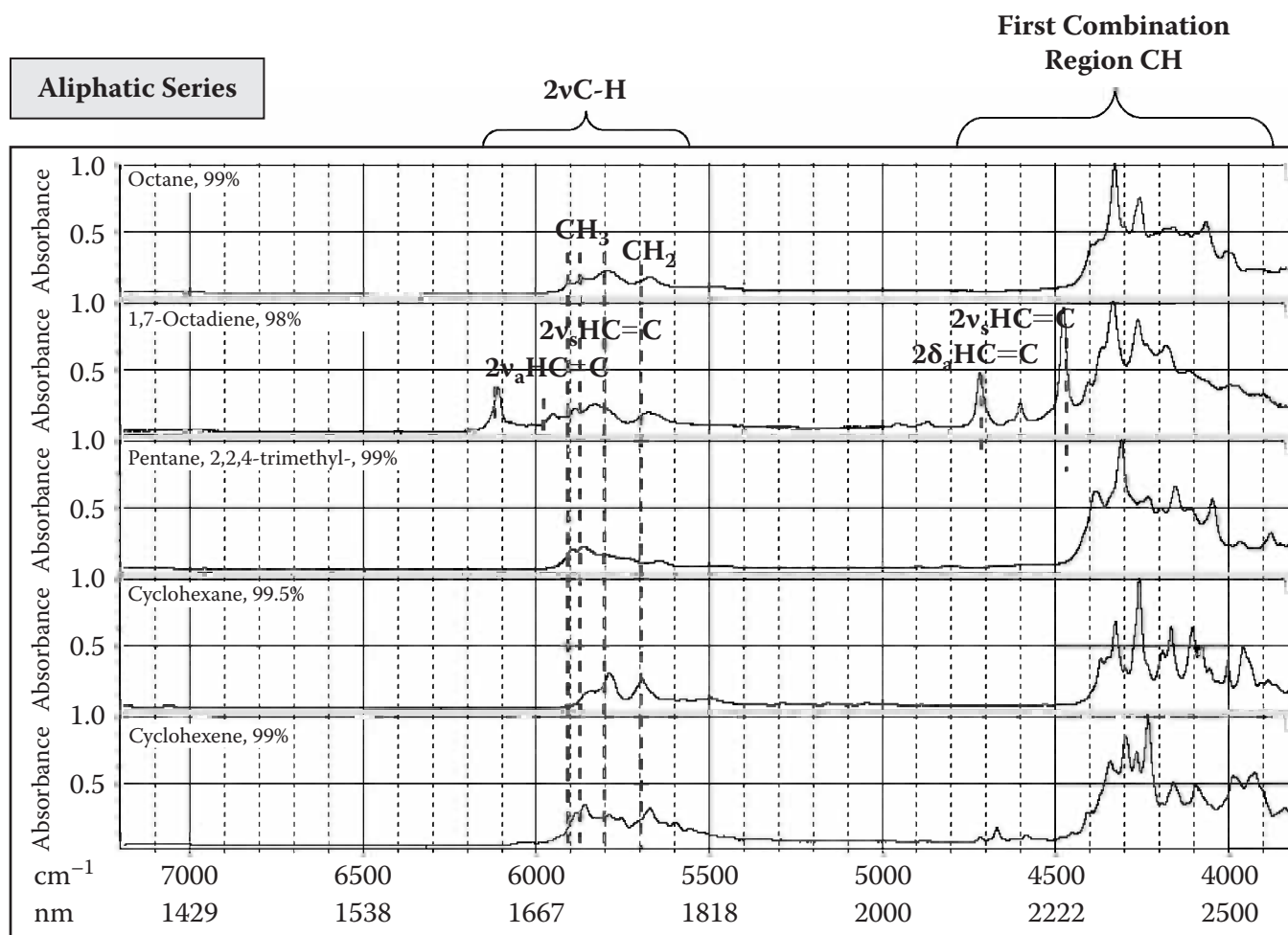


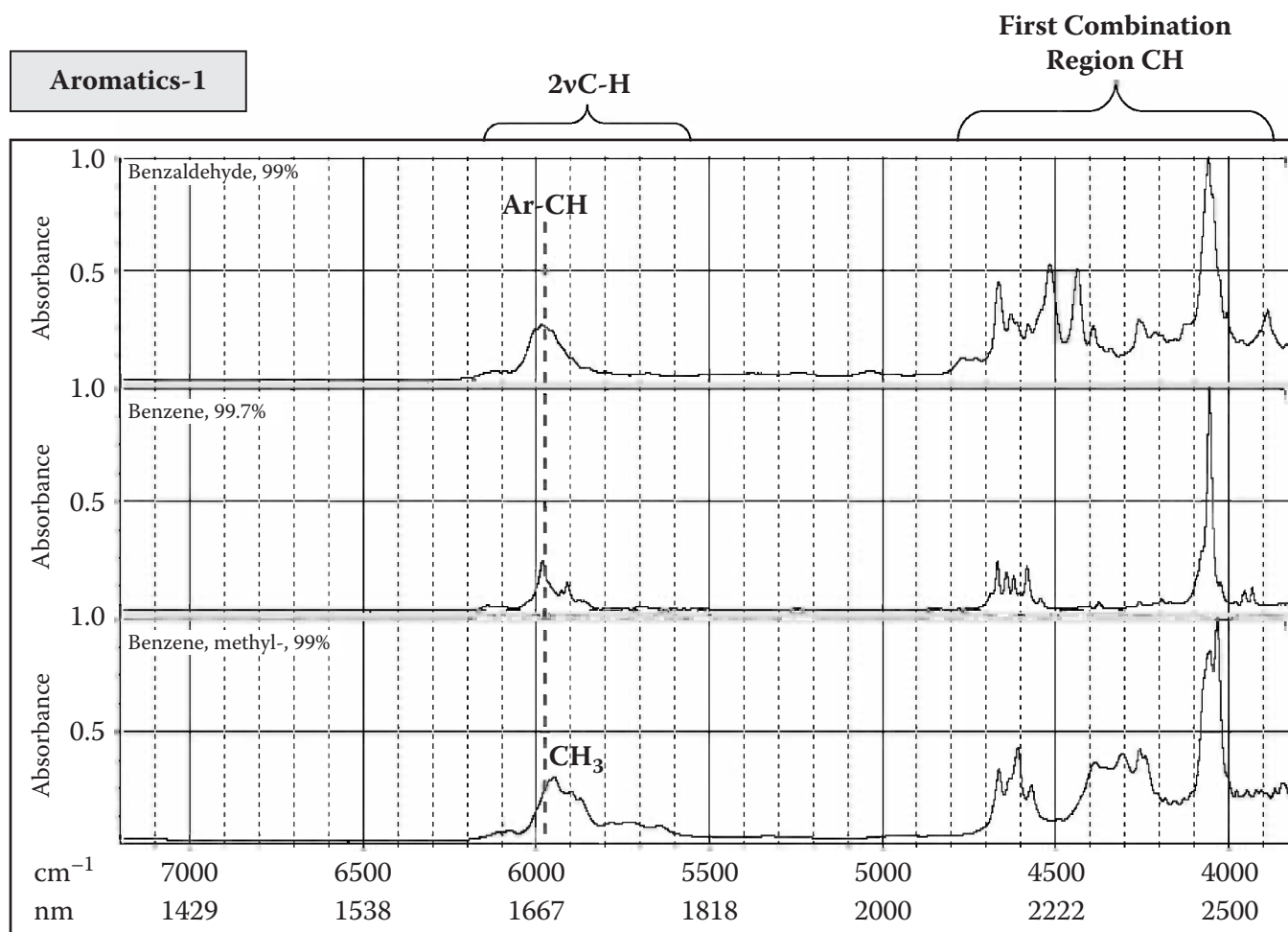


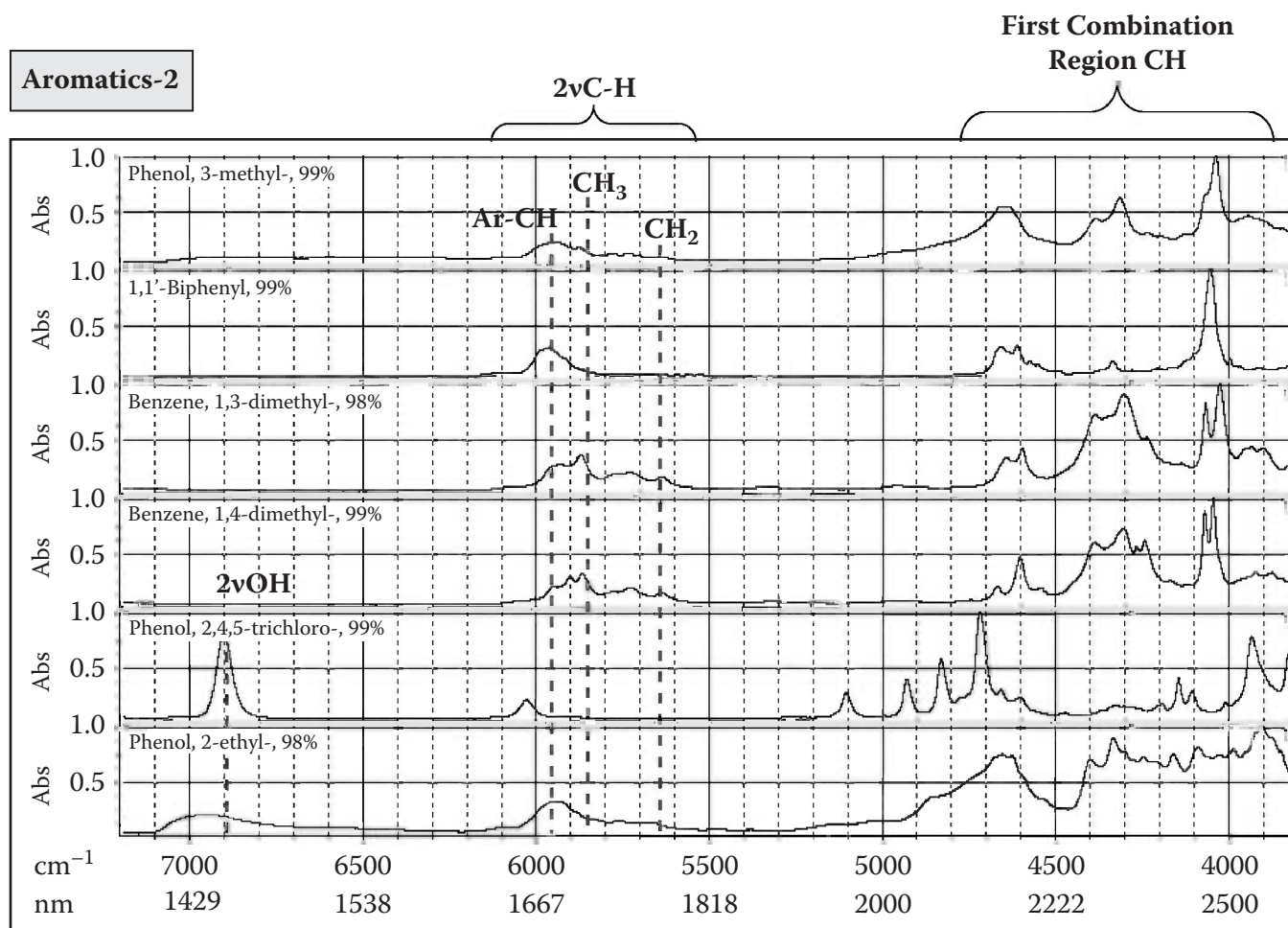


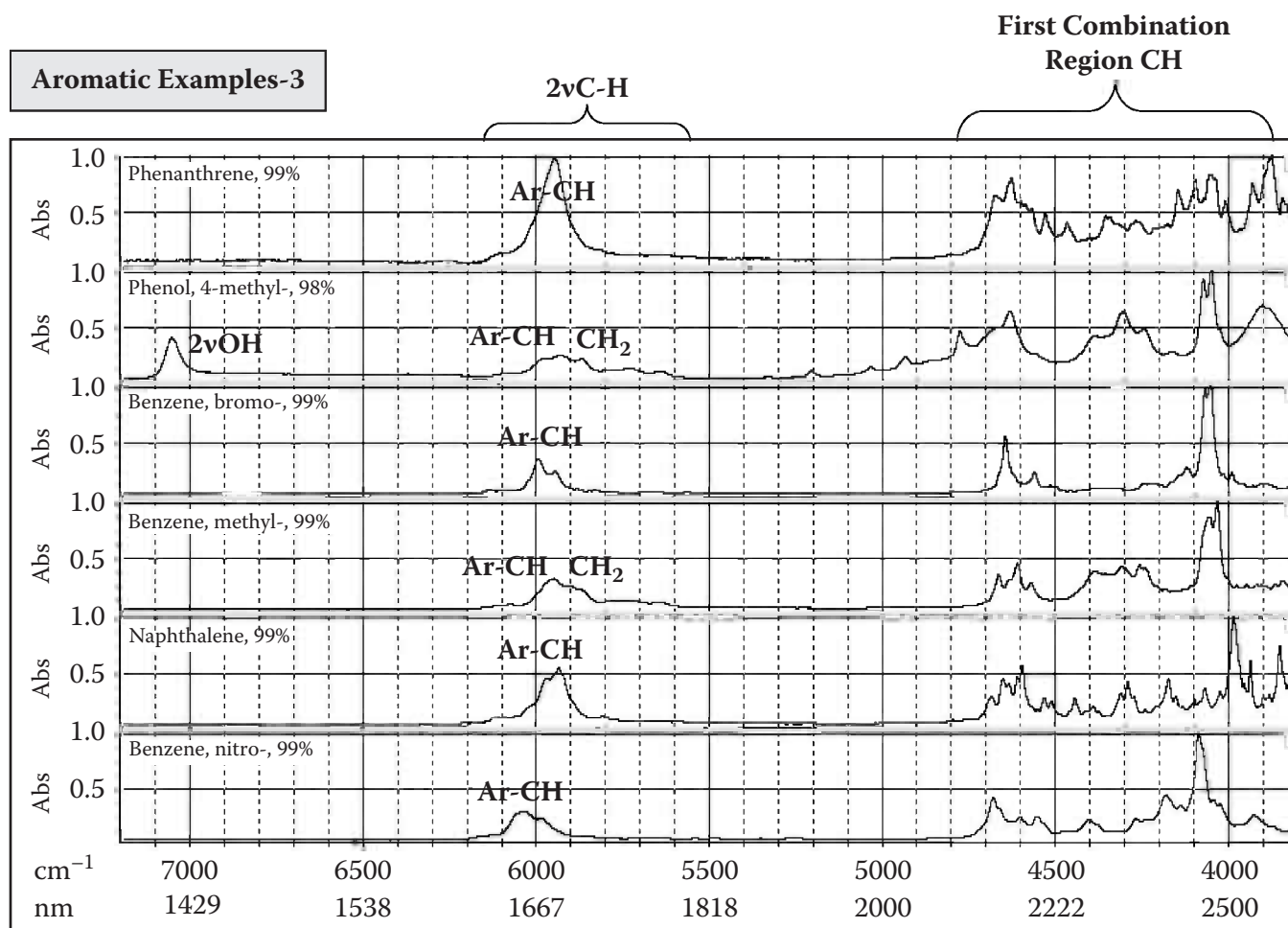


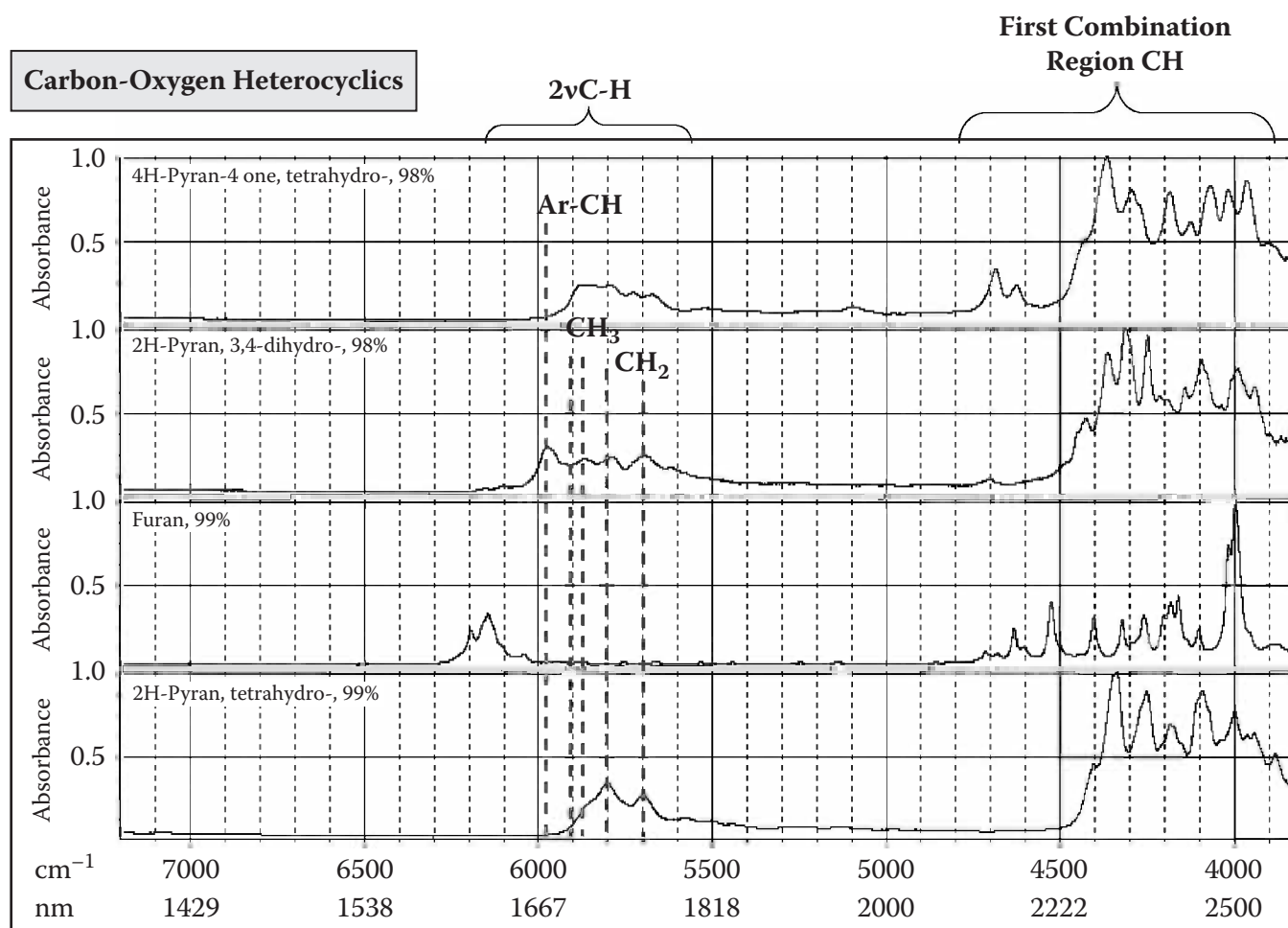




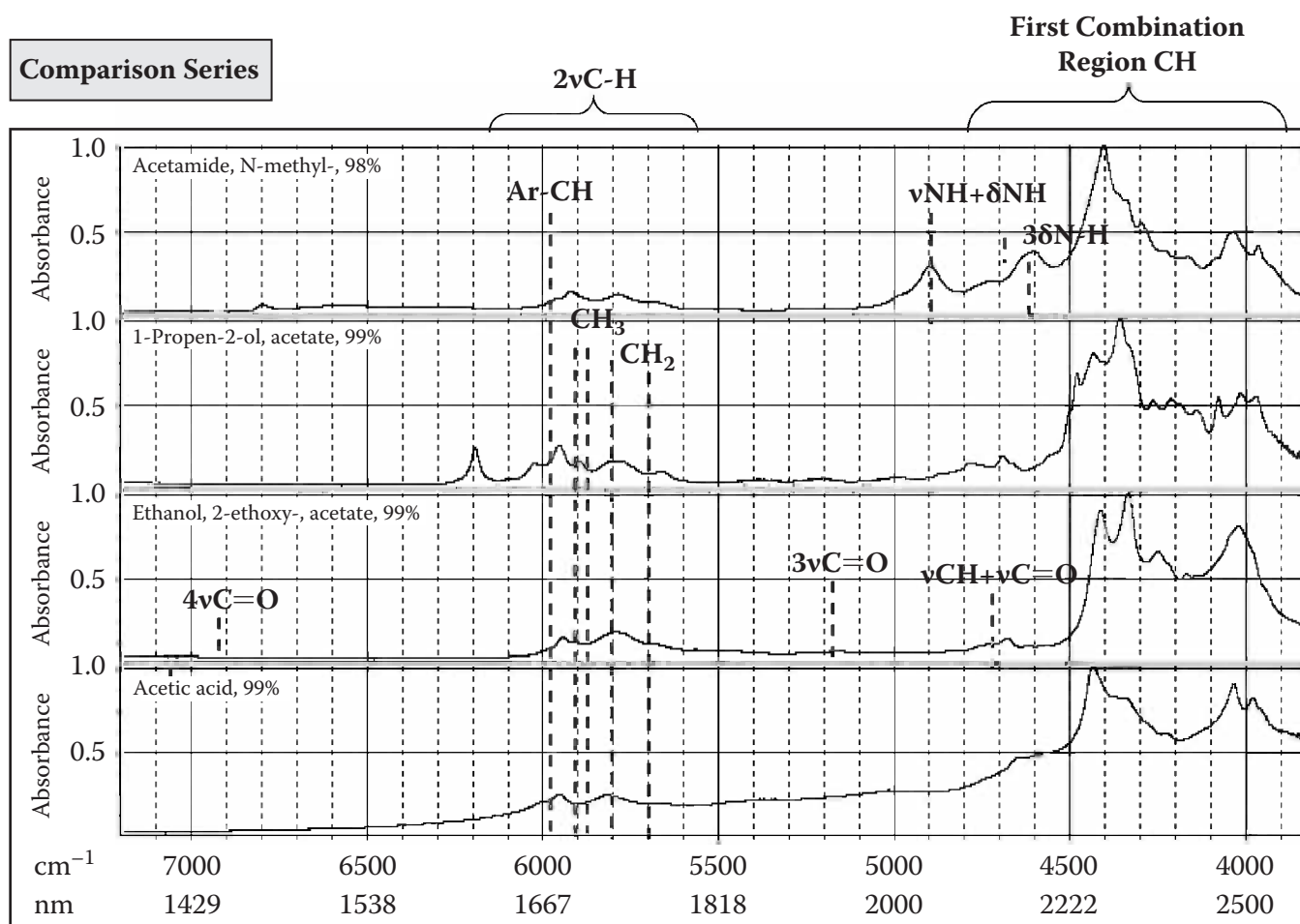


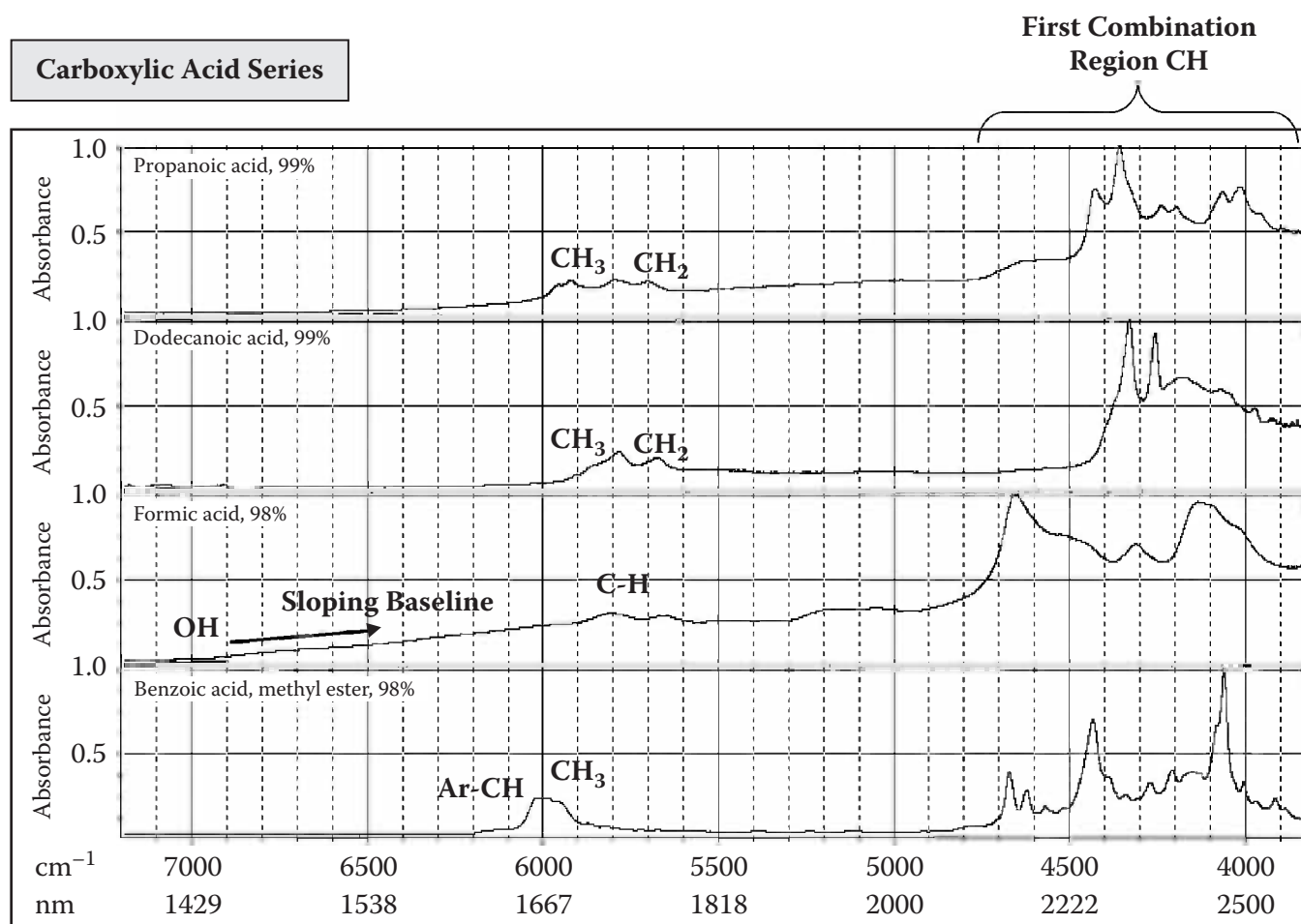


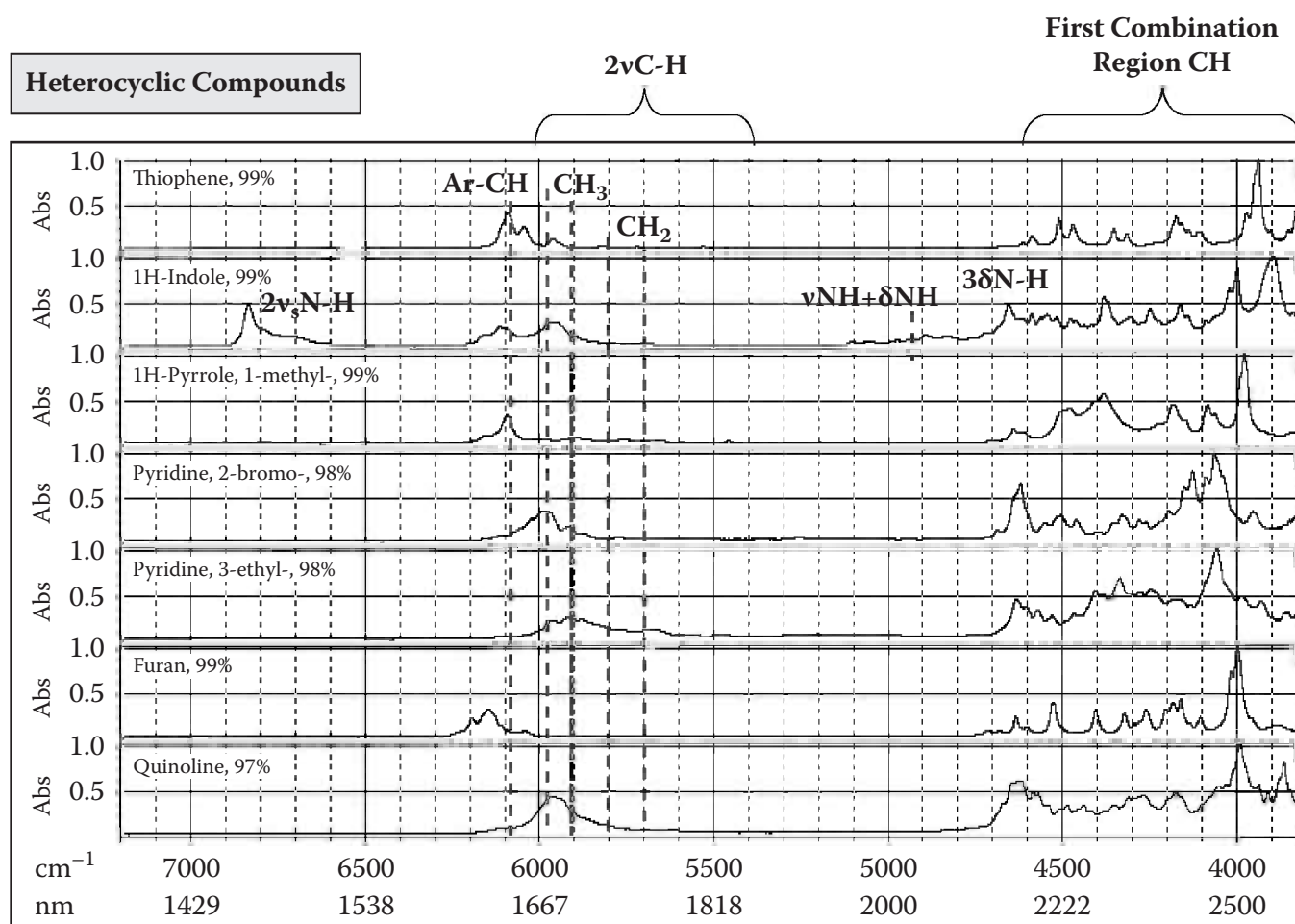


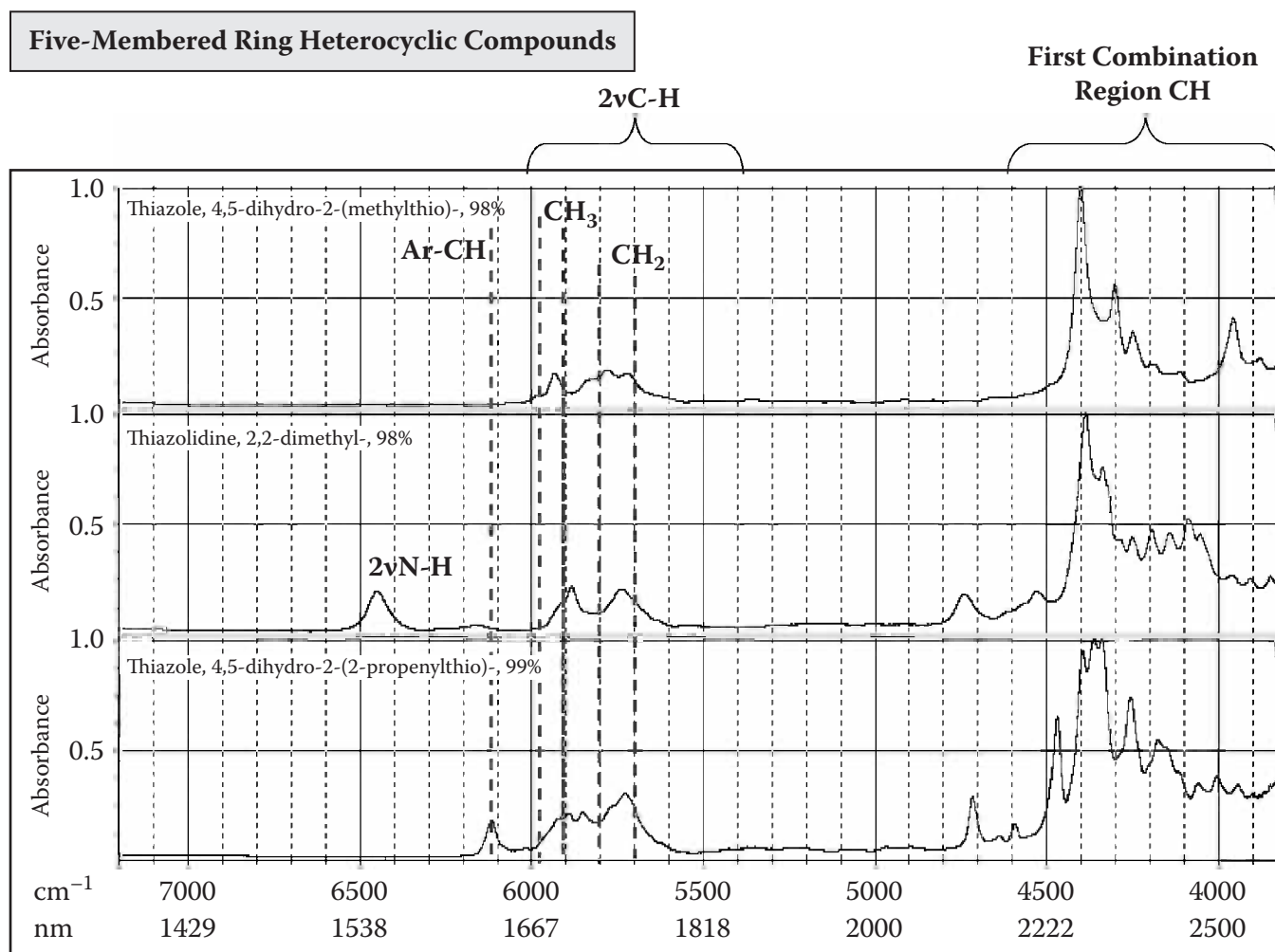


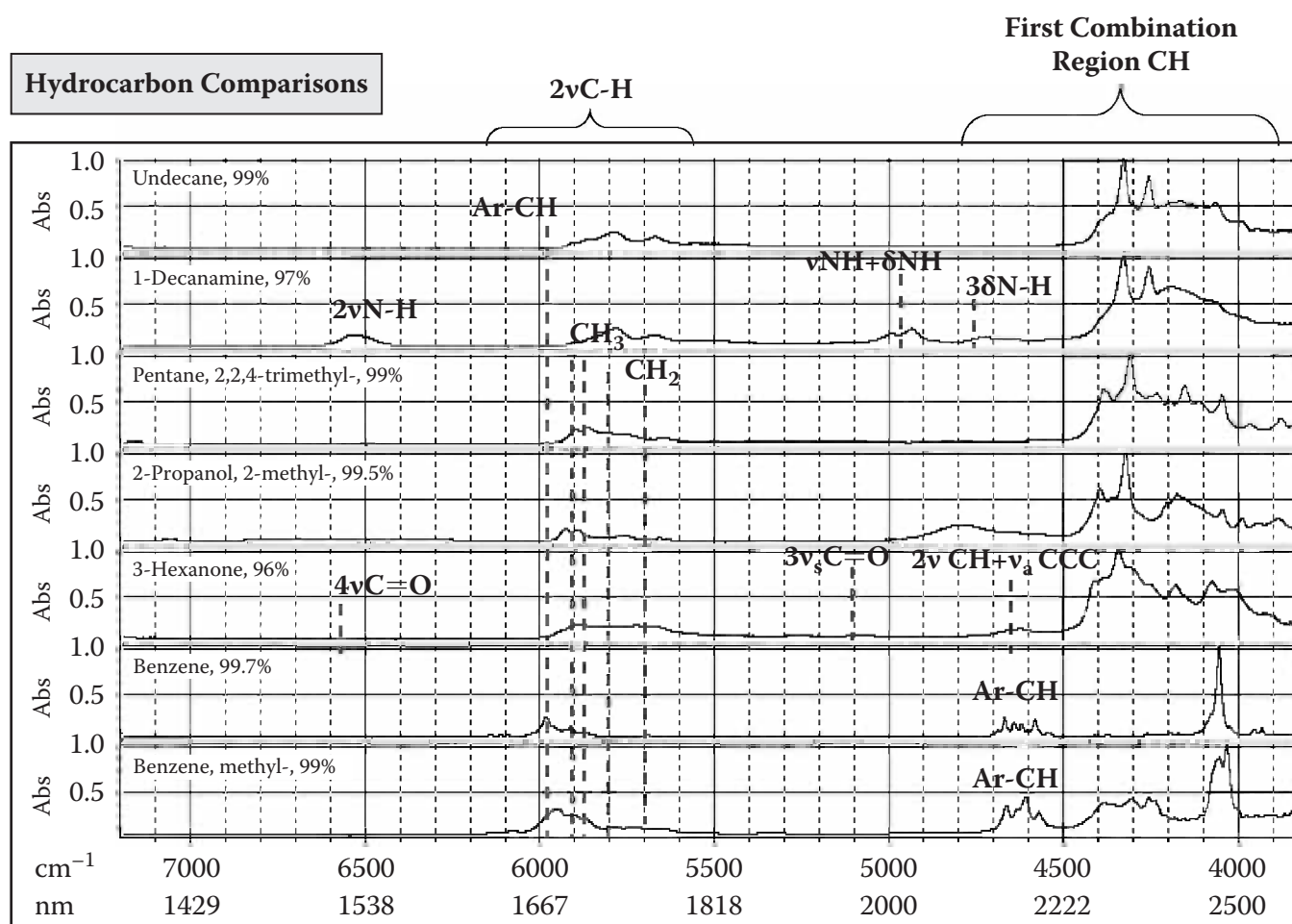


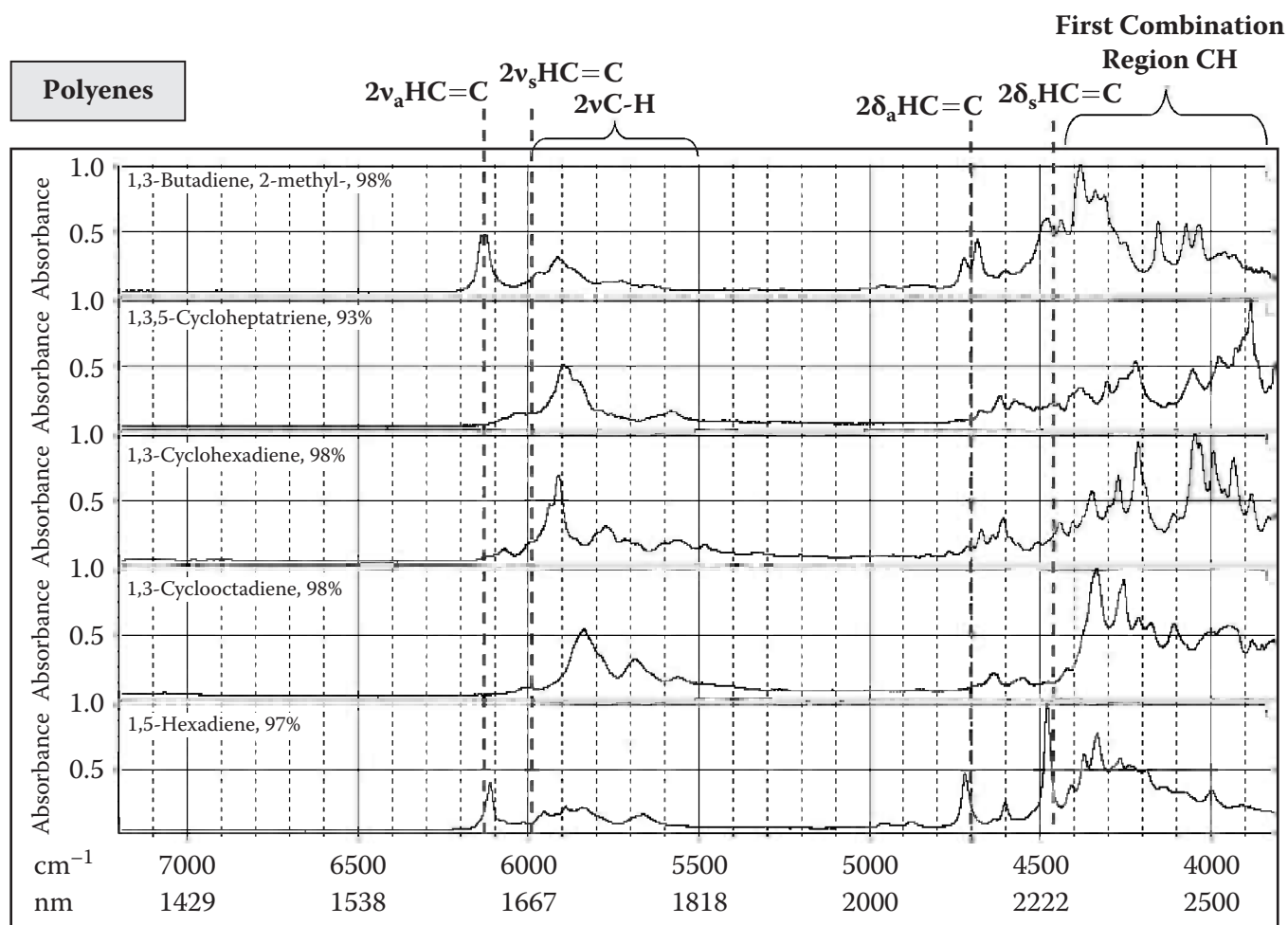


















# Appendix C

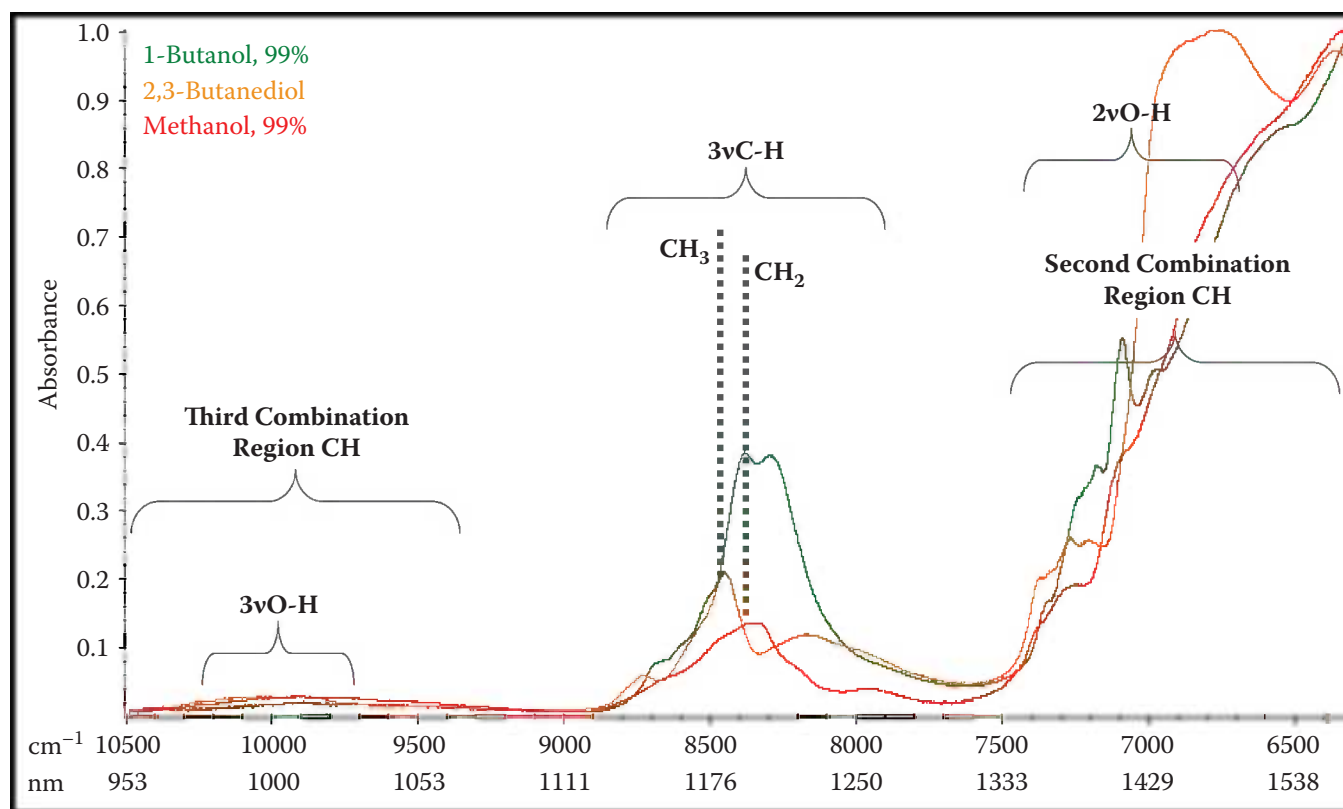
## Detailed Spectra–Structure Correlations\*

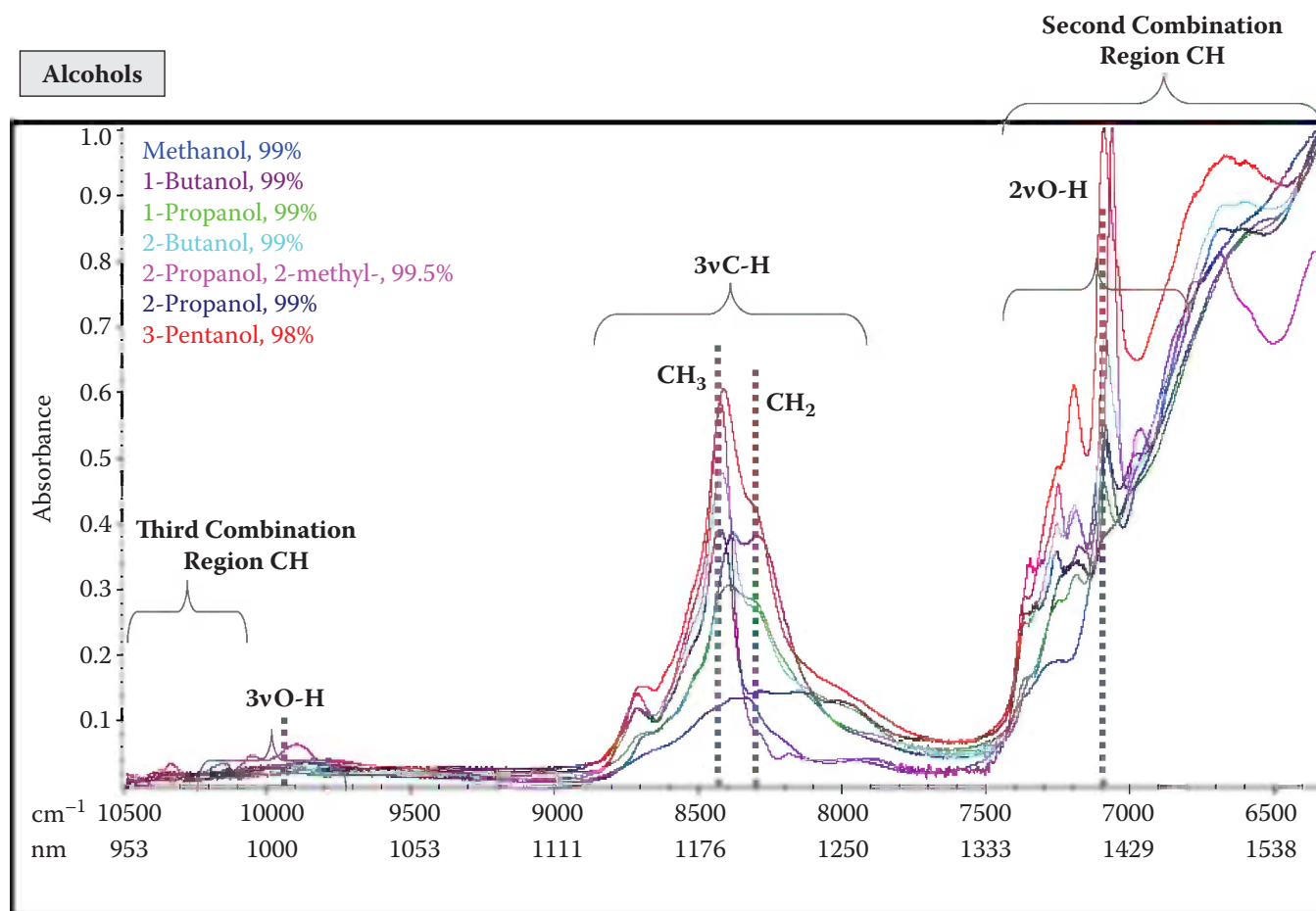
*Overlapping Spectra from  
10500 cm<sup>-1</sup> to 3800 cm<sup>-1</sup>  
(952 nm to 2632 nm)*

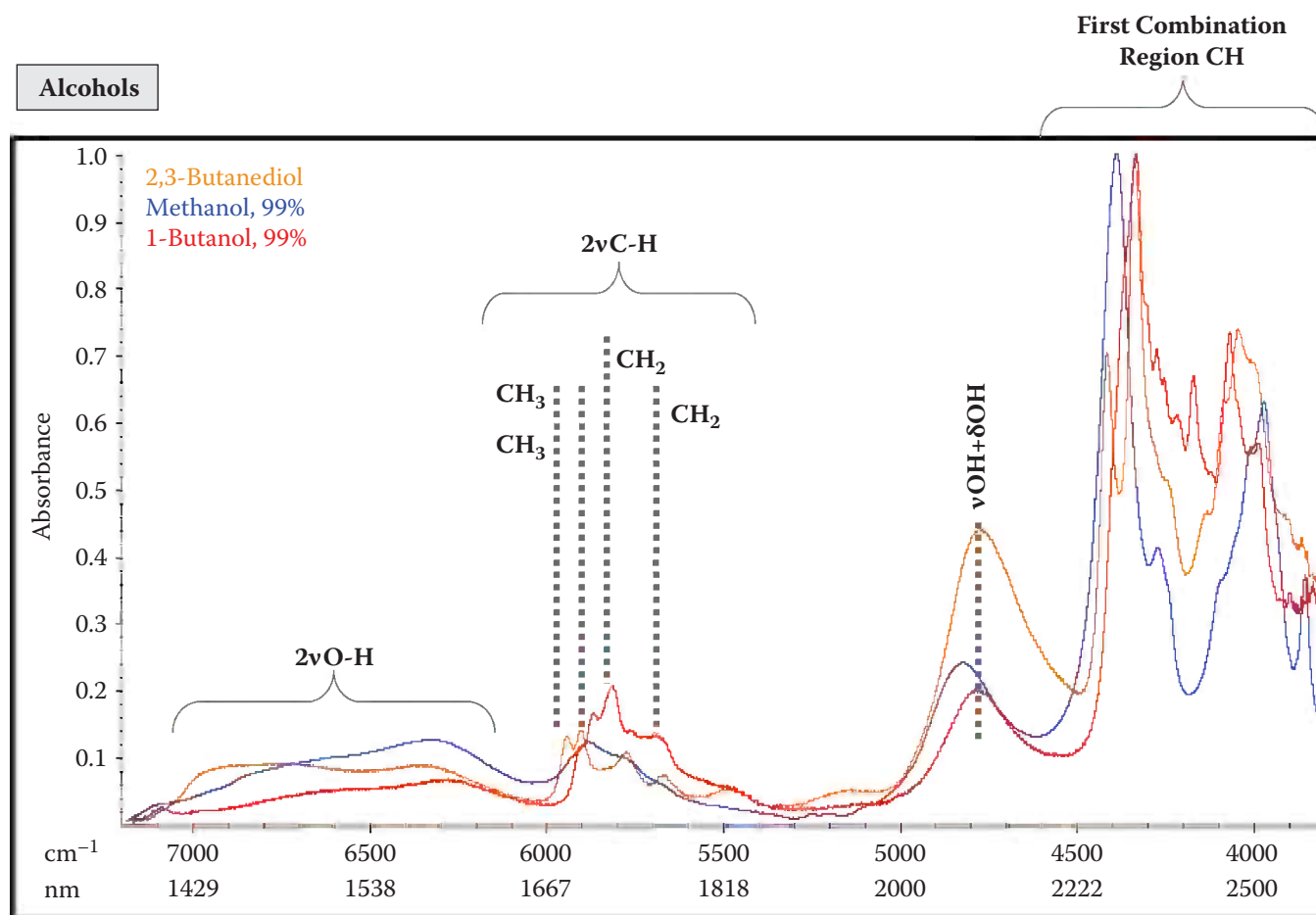
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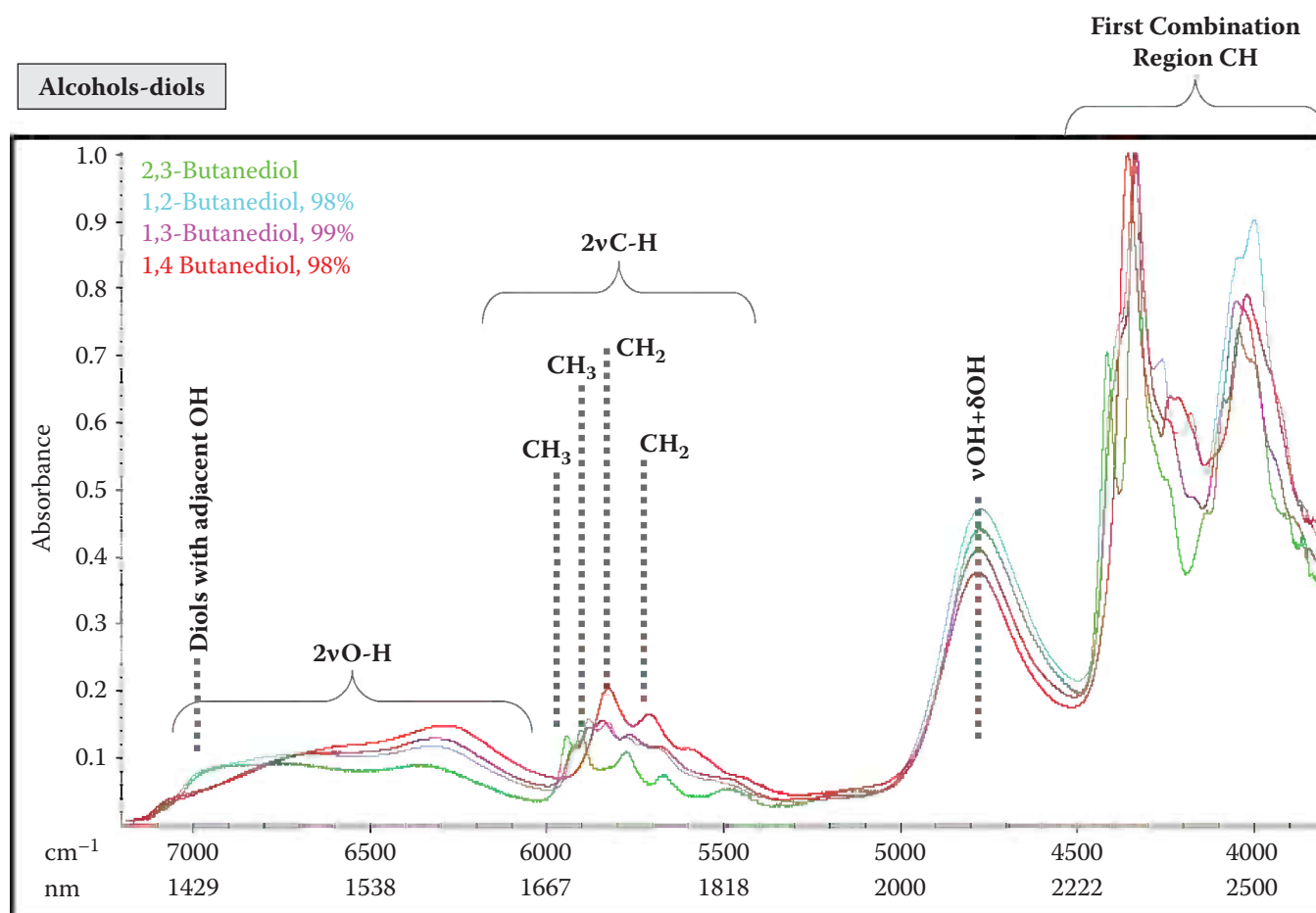
\* Spectra used by permission “NIR Spectra of Organic Compounds,” © Wiley-VCH, ISBN 3-527-31630-2.

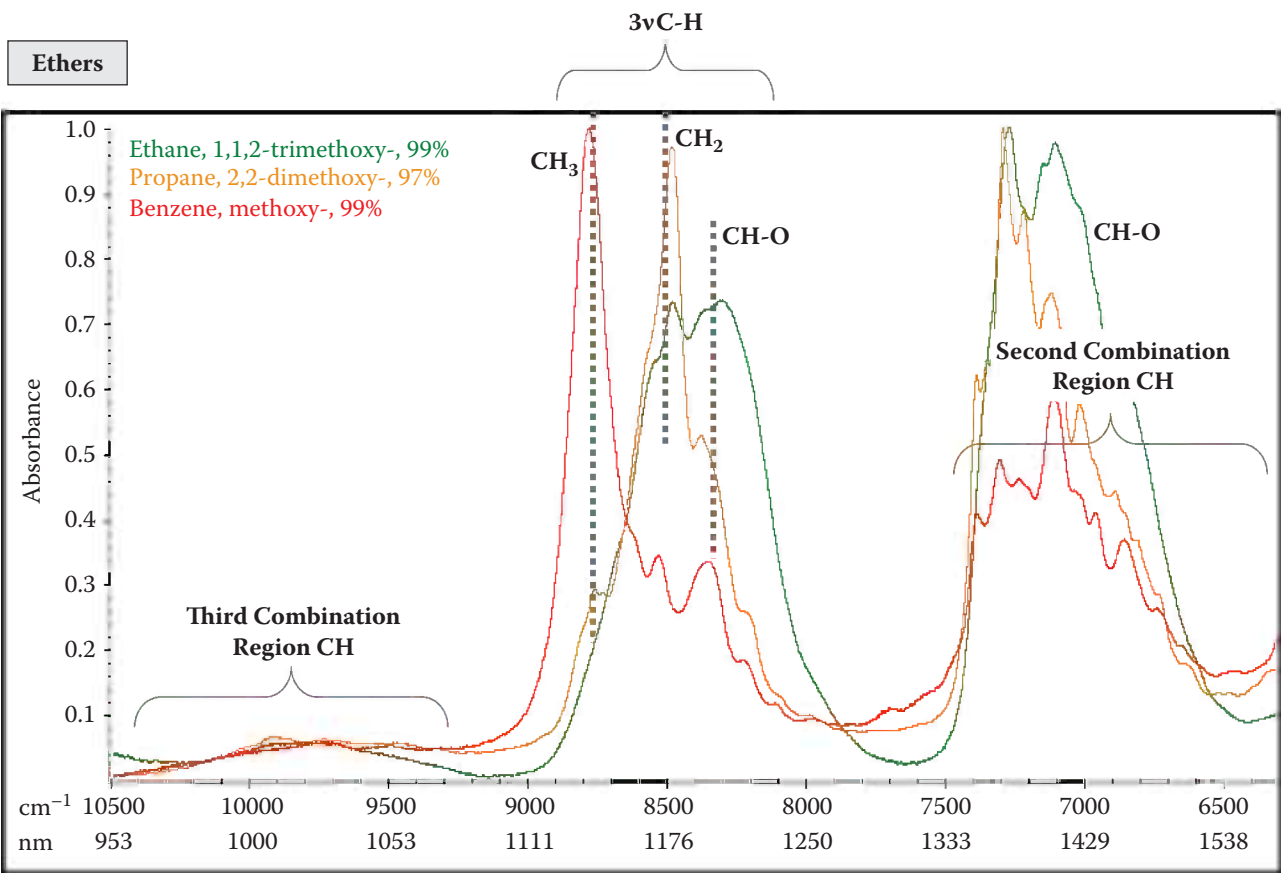
## Alcohols



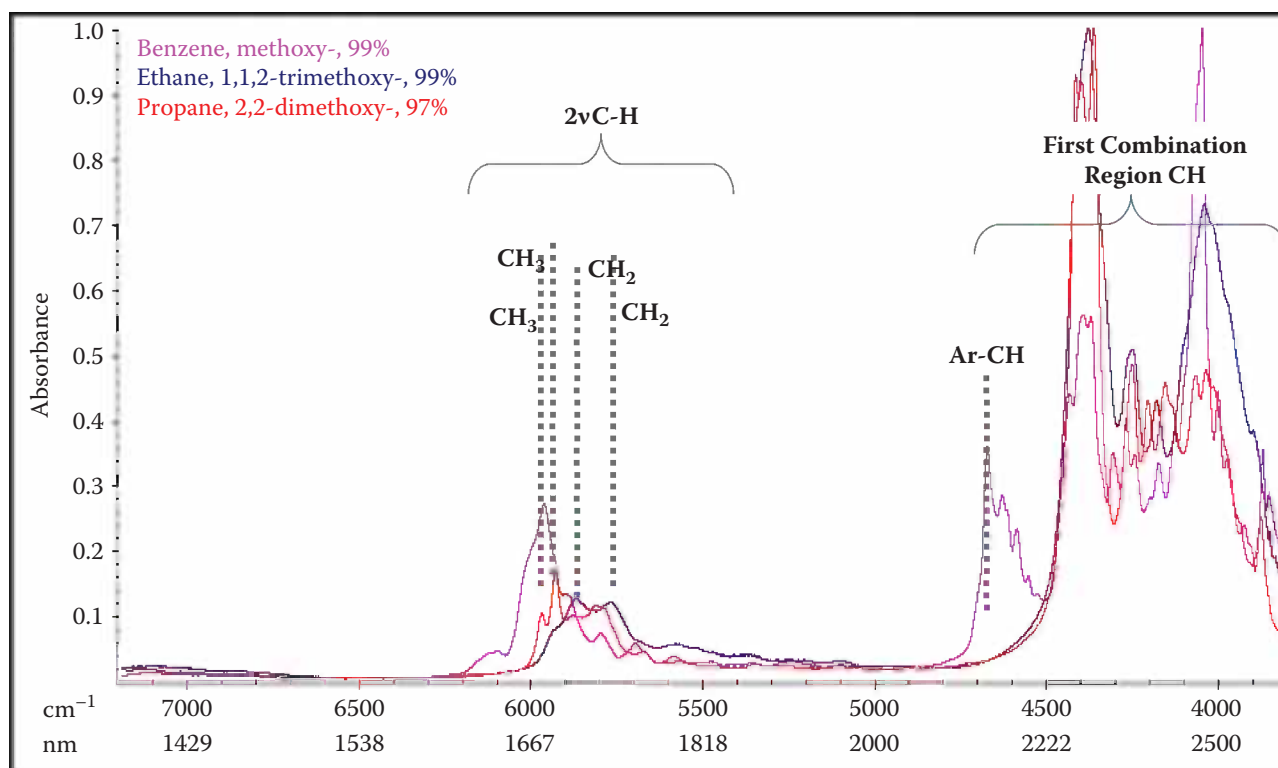


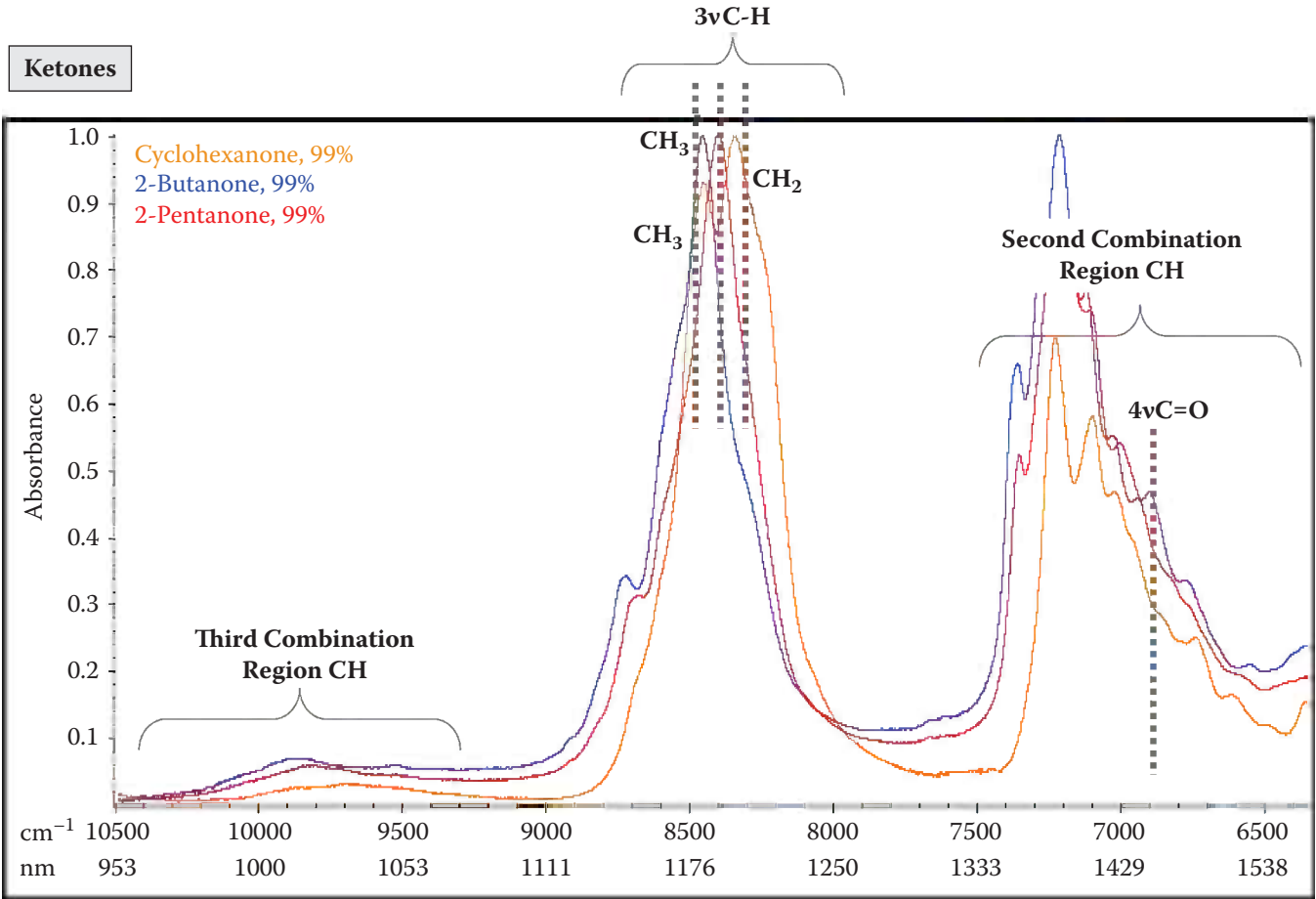






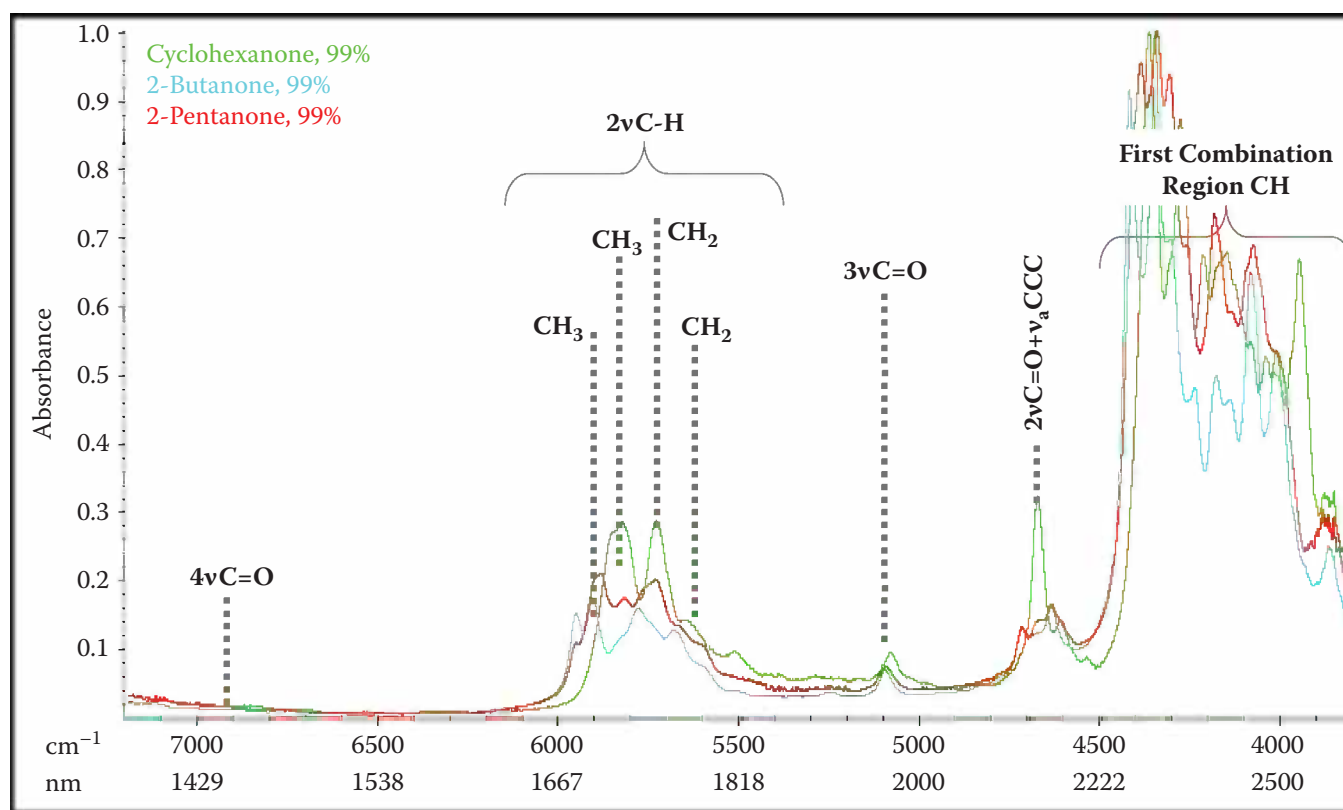
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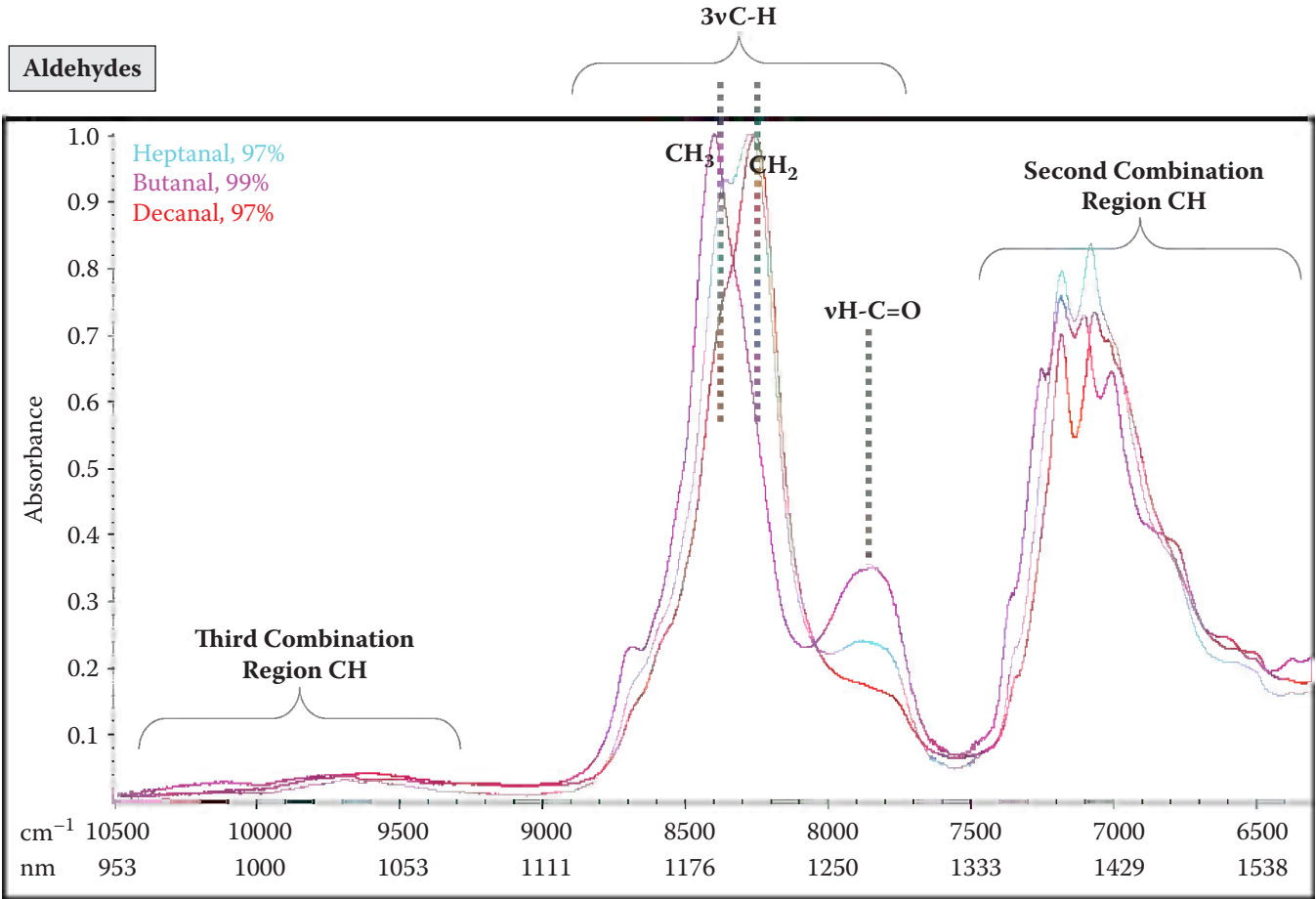




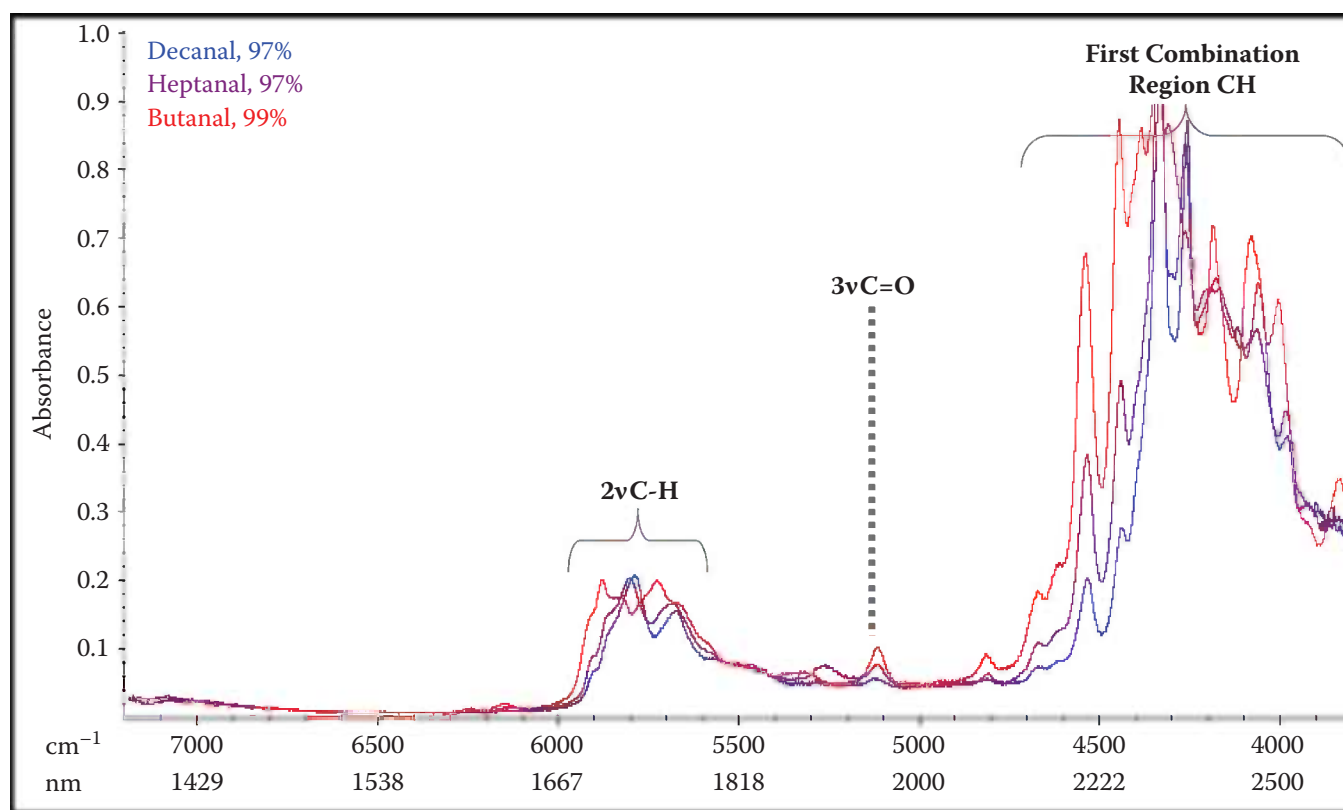


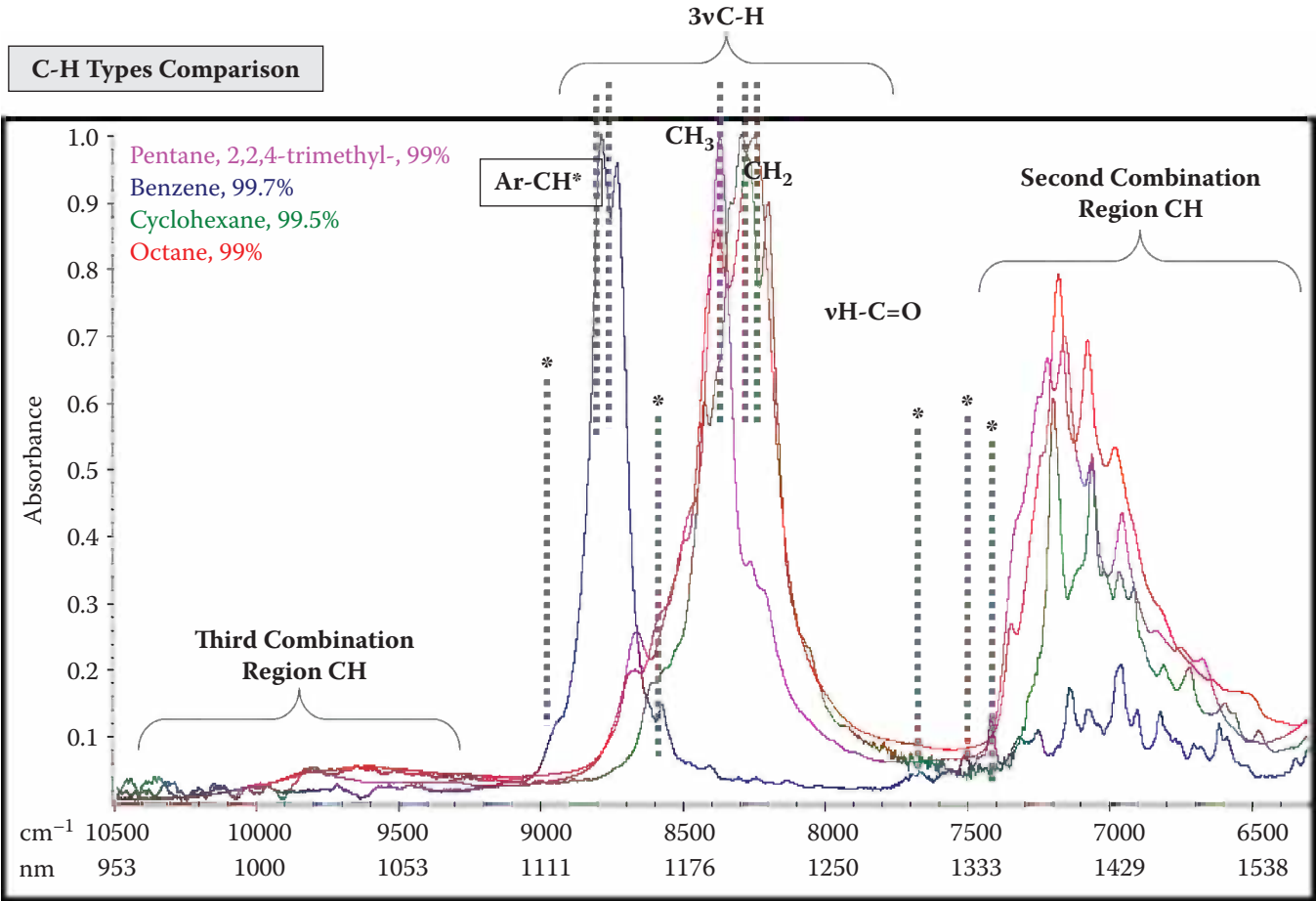
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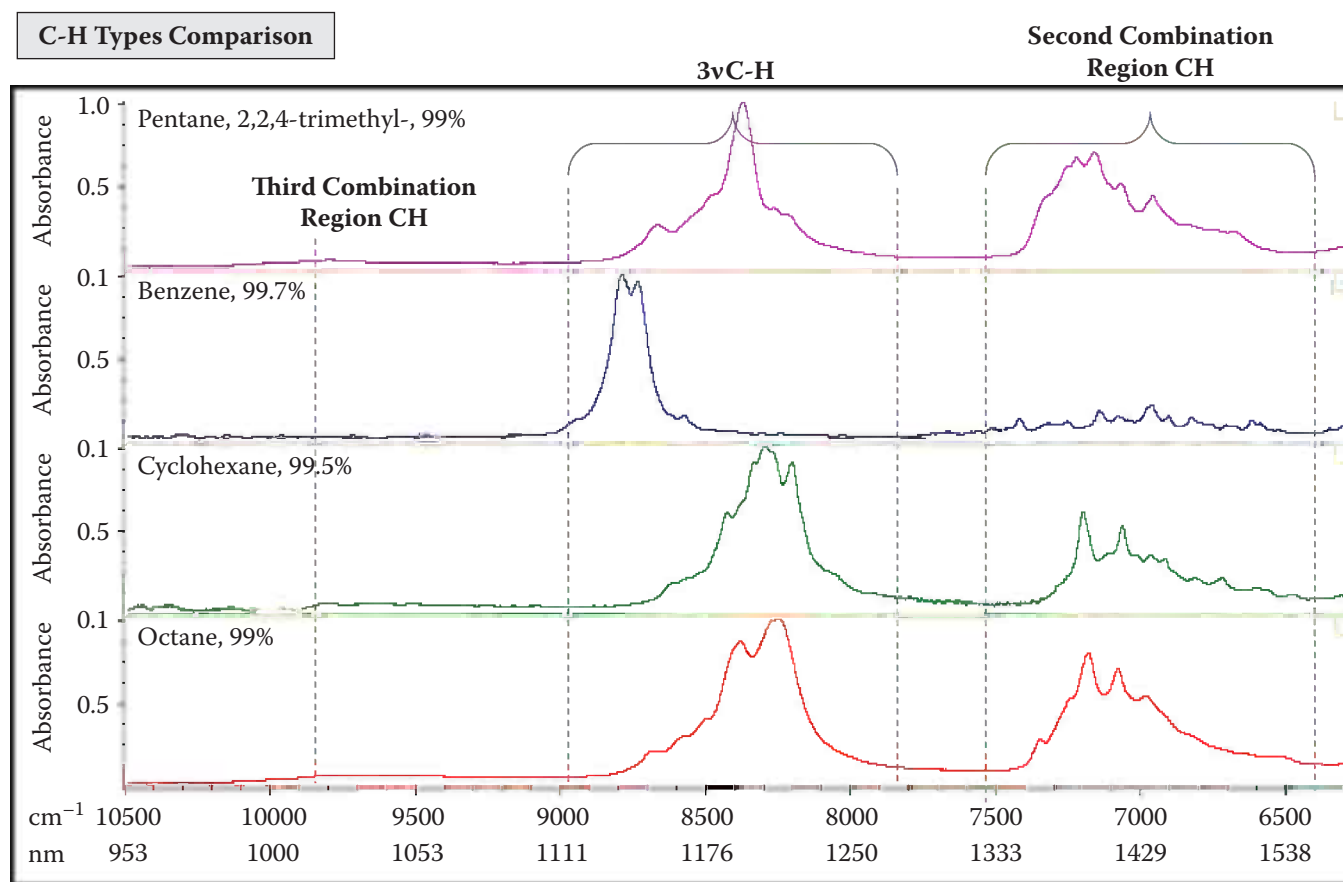


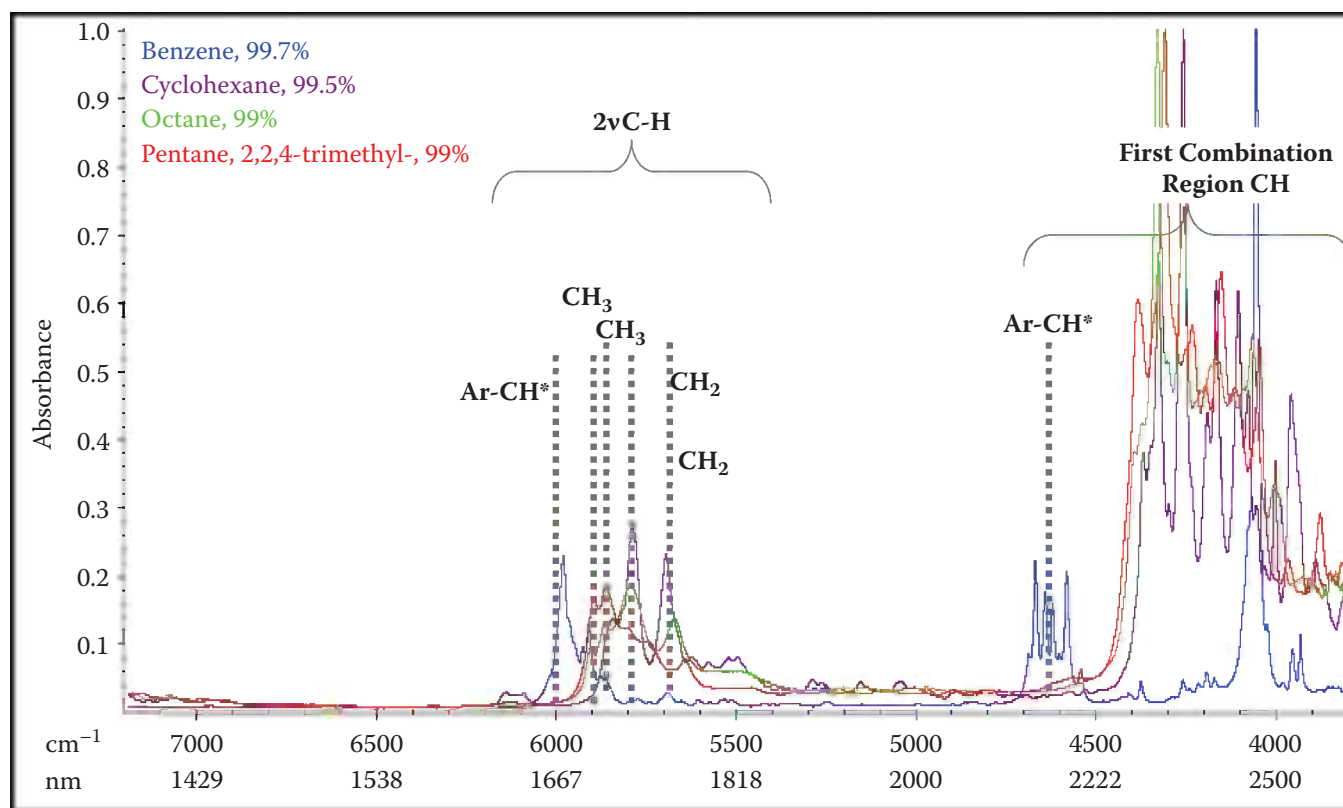


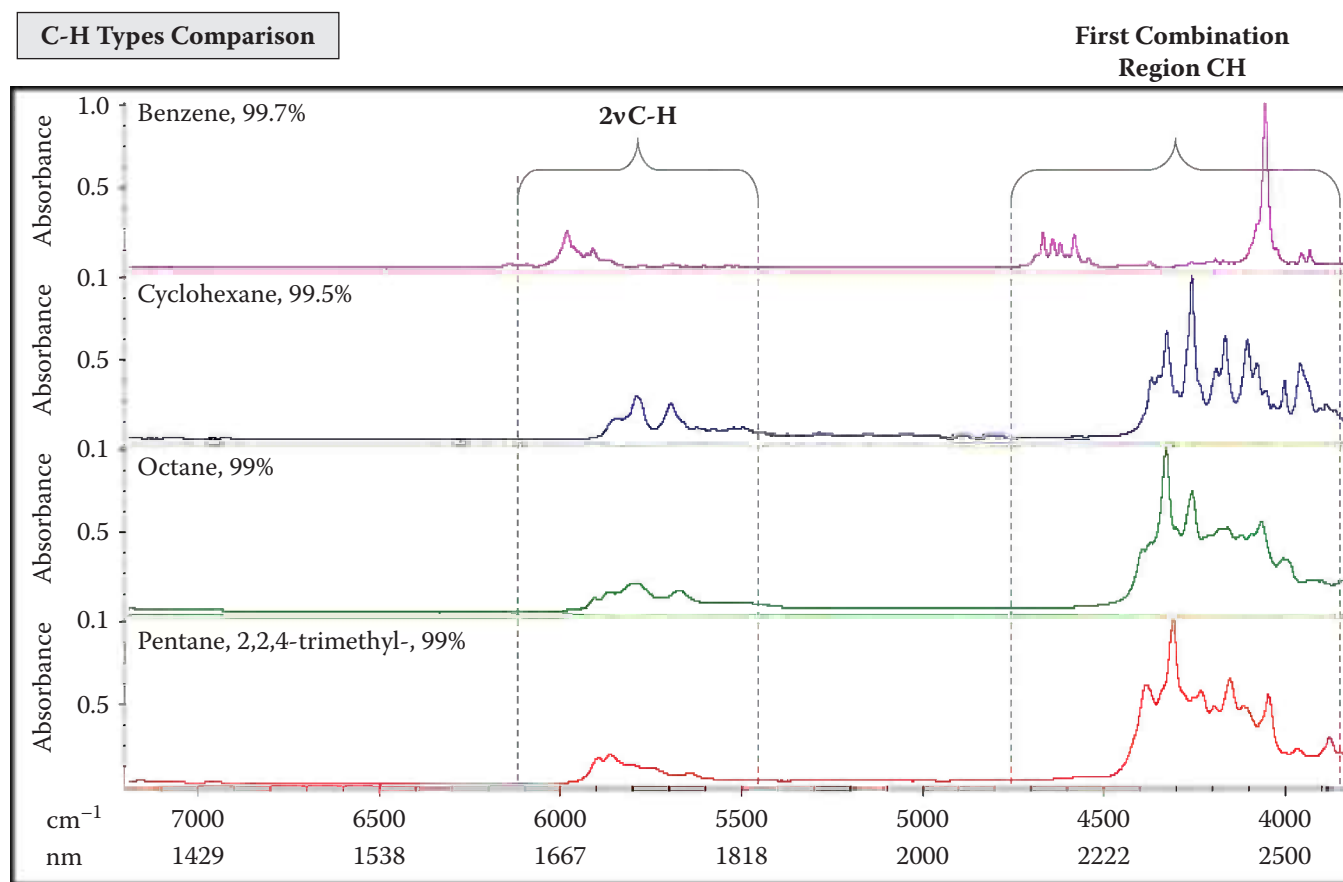
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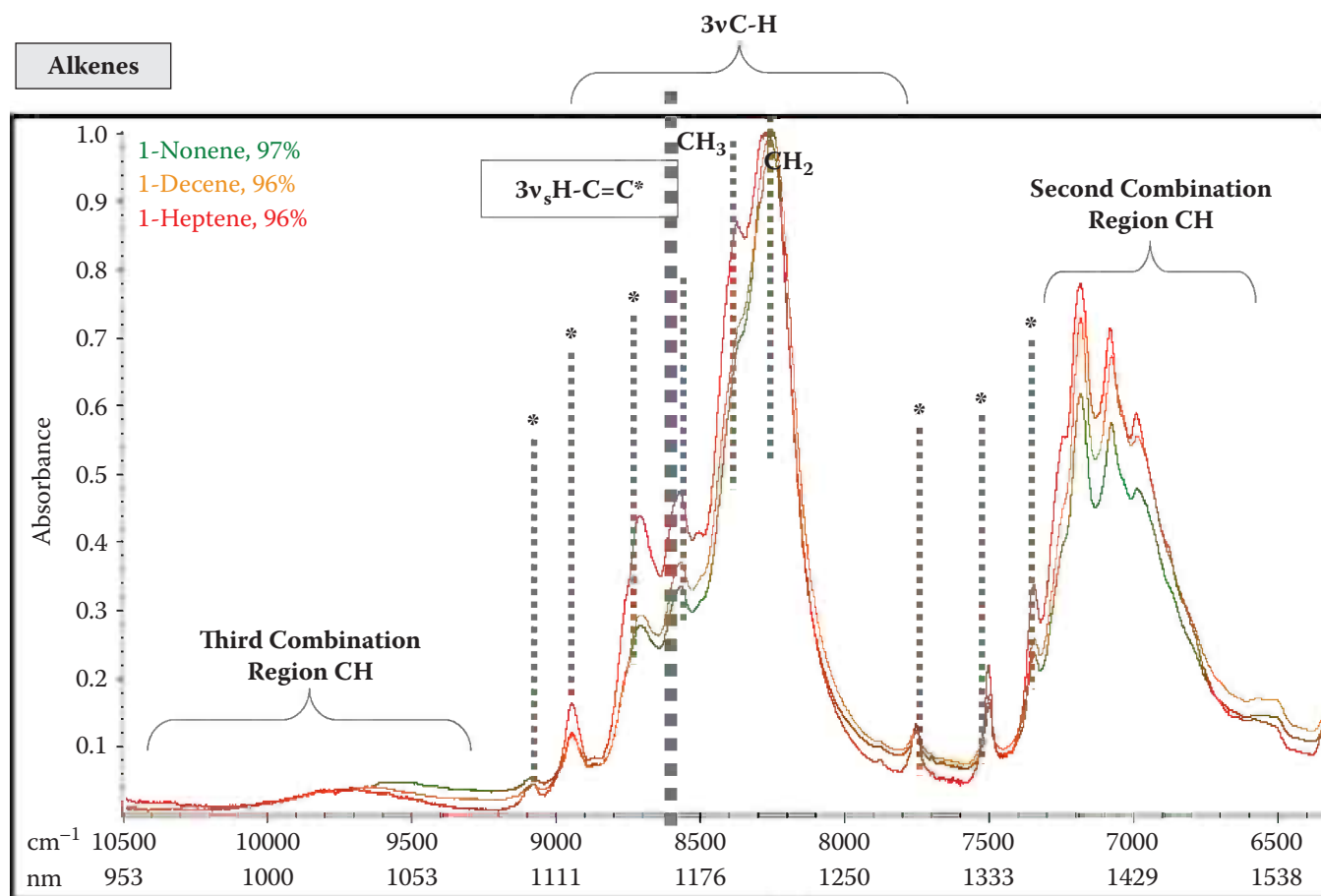






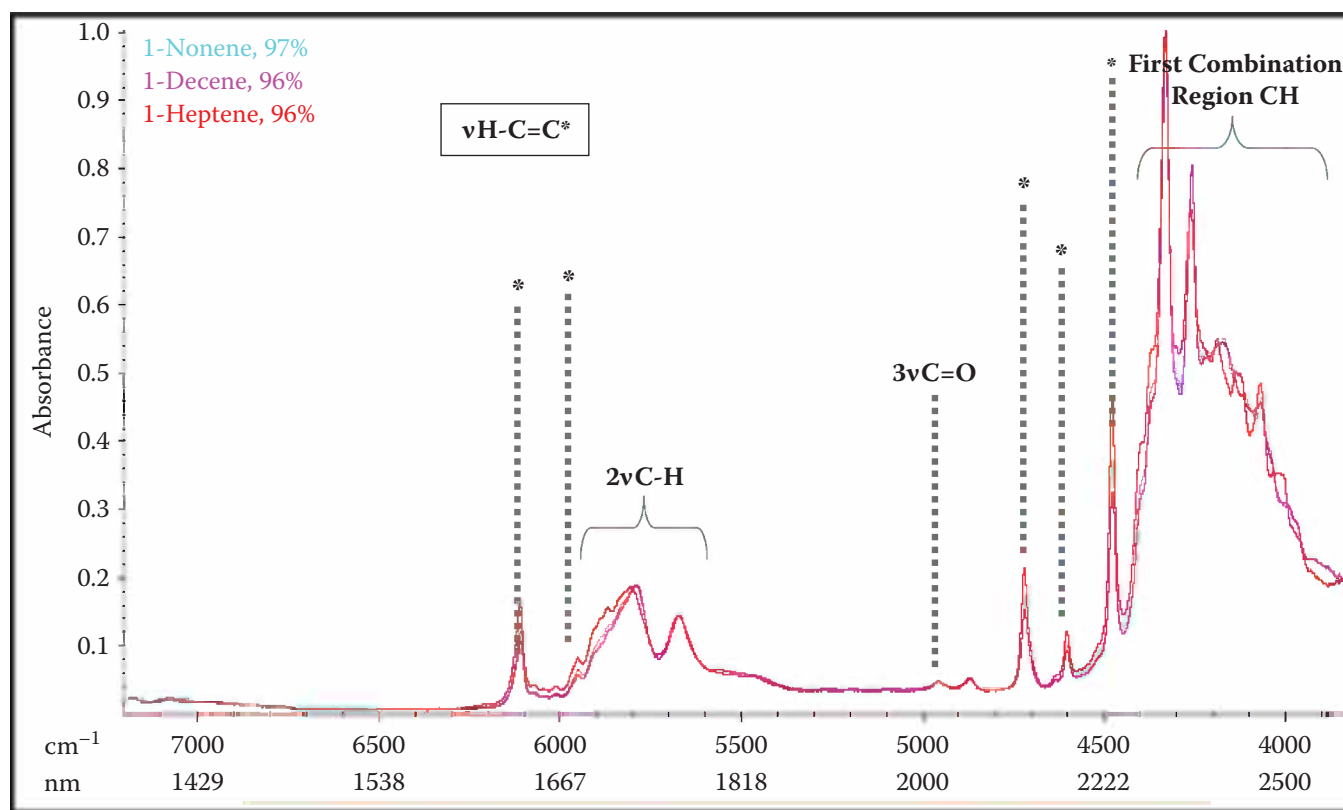
**C-H Types Comparison**



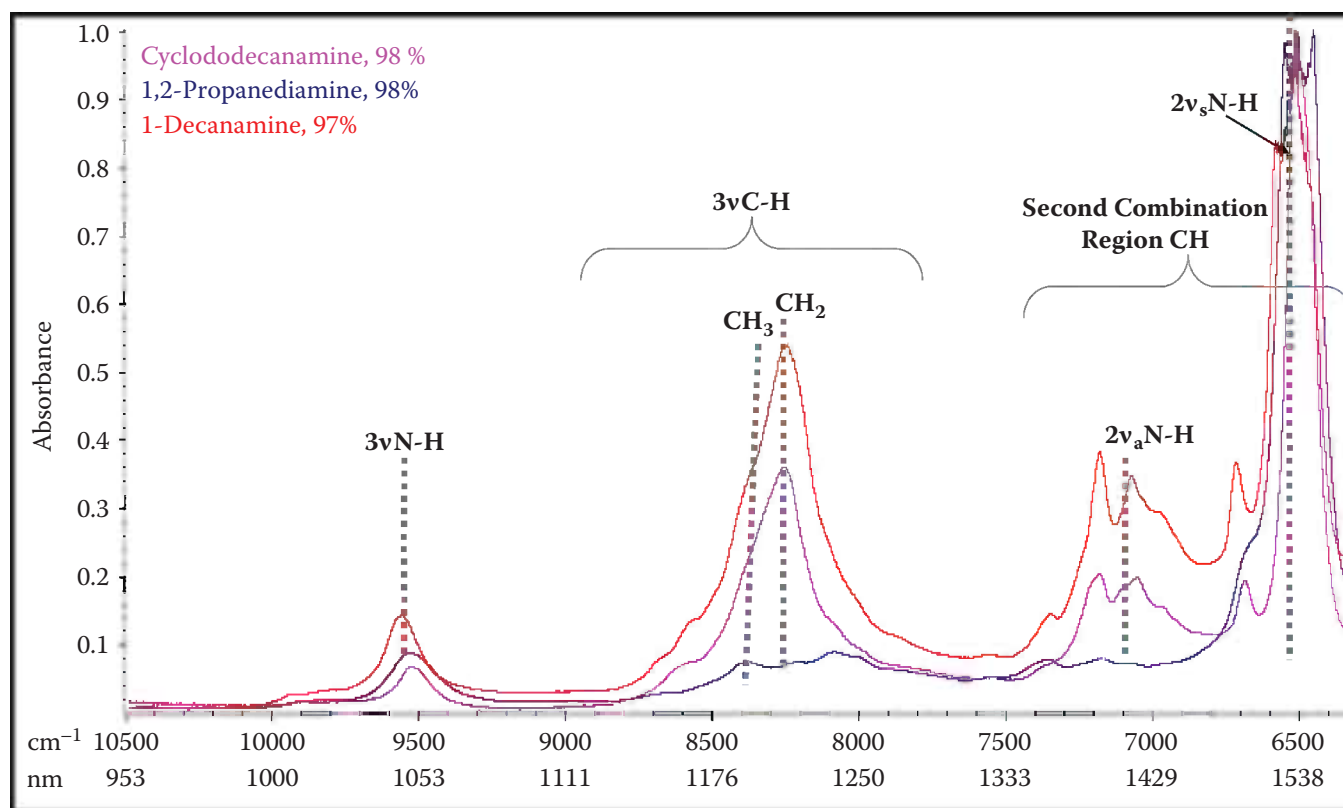




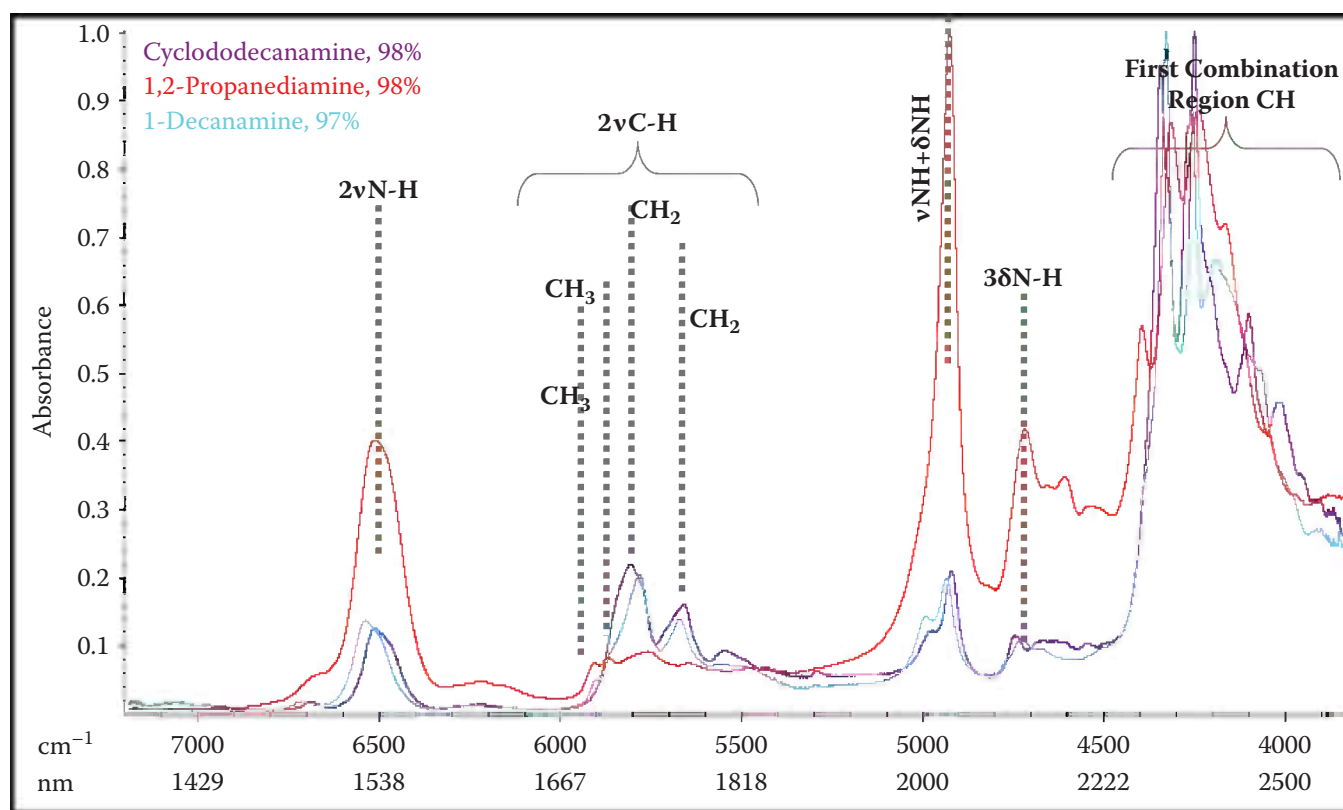
## Alkenes



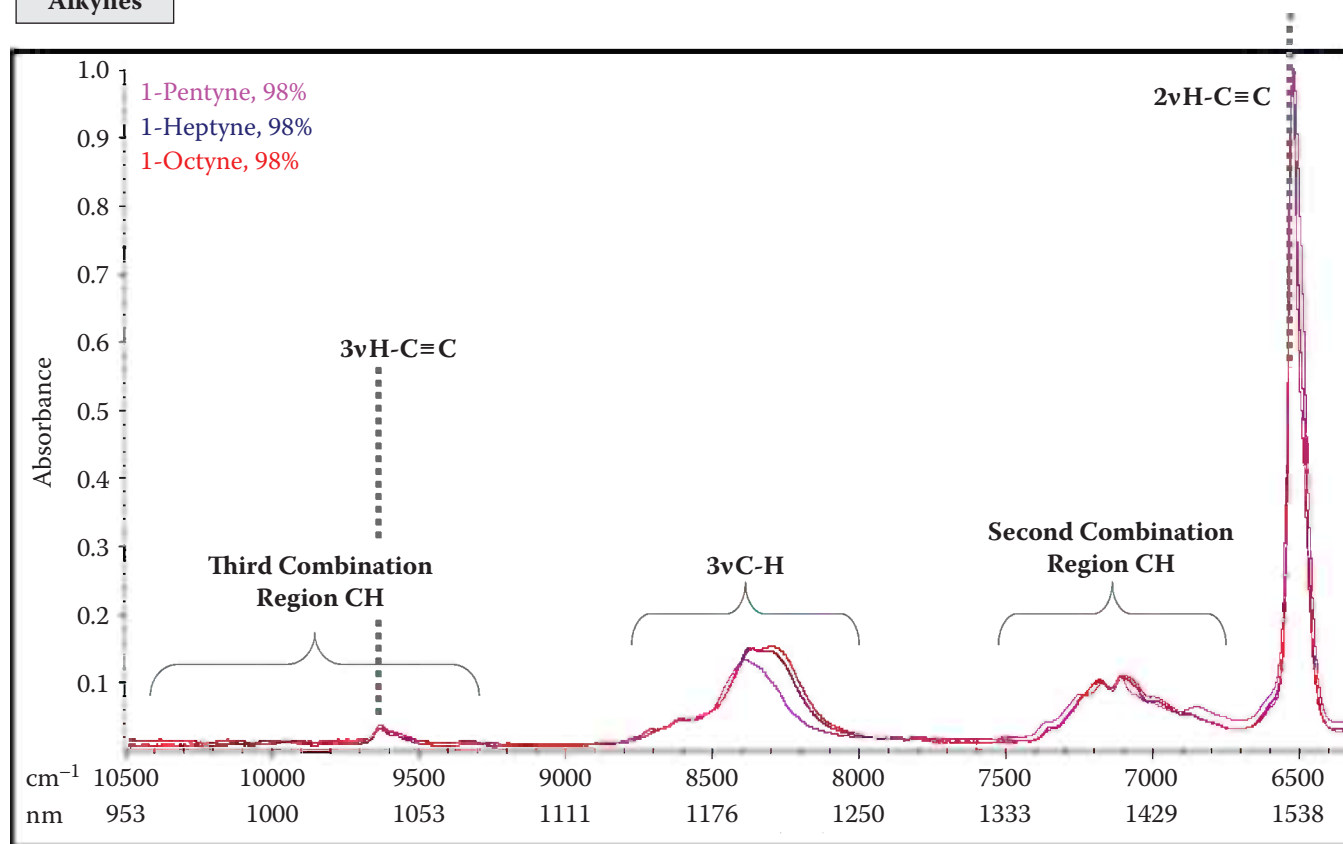
## Amines



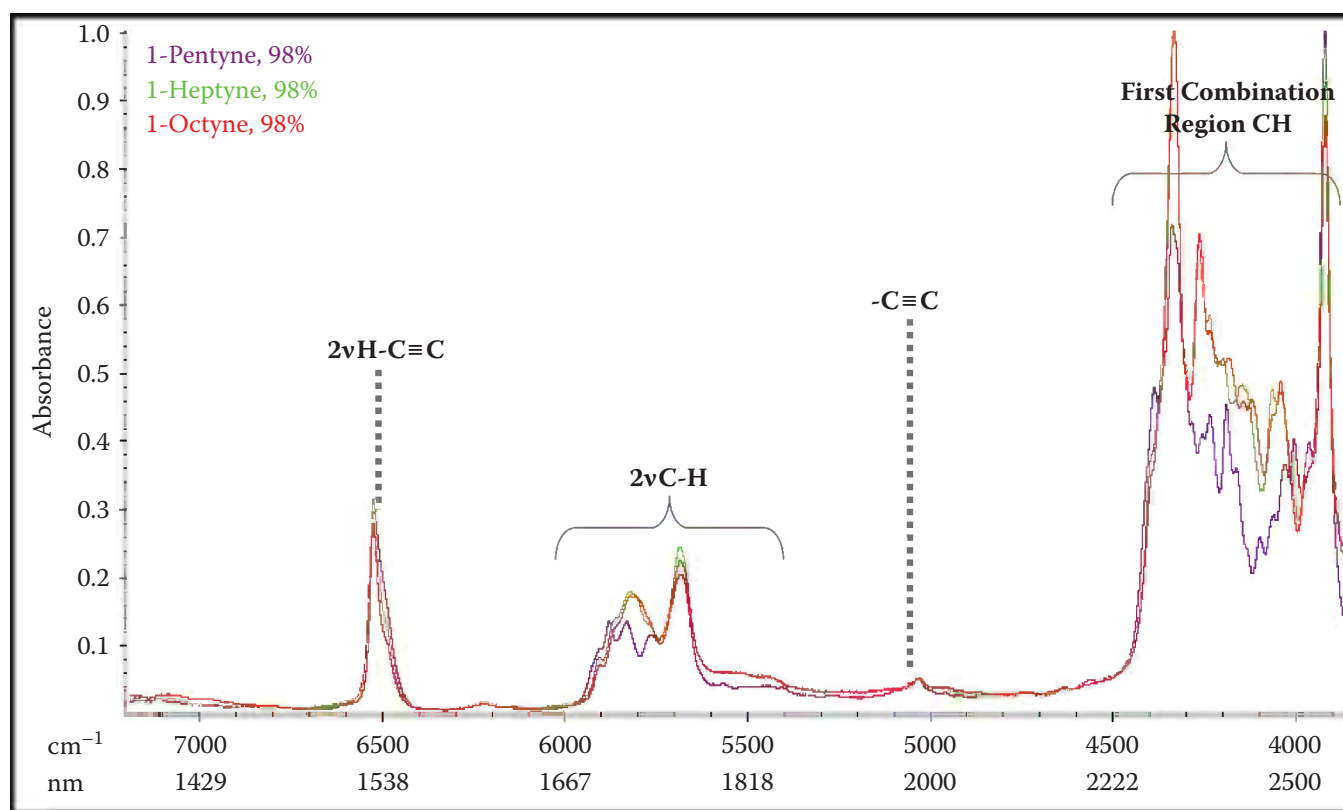
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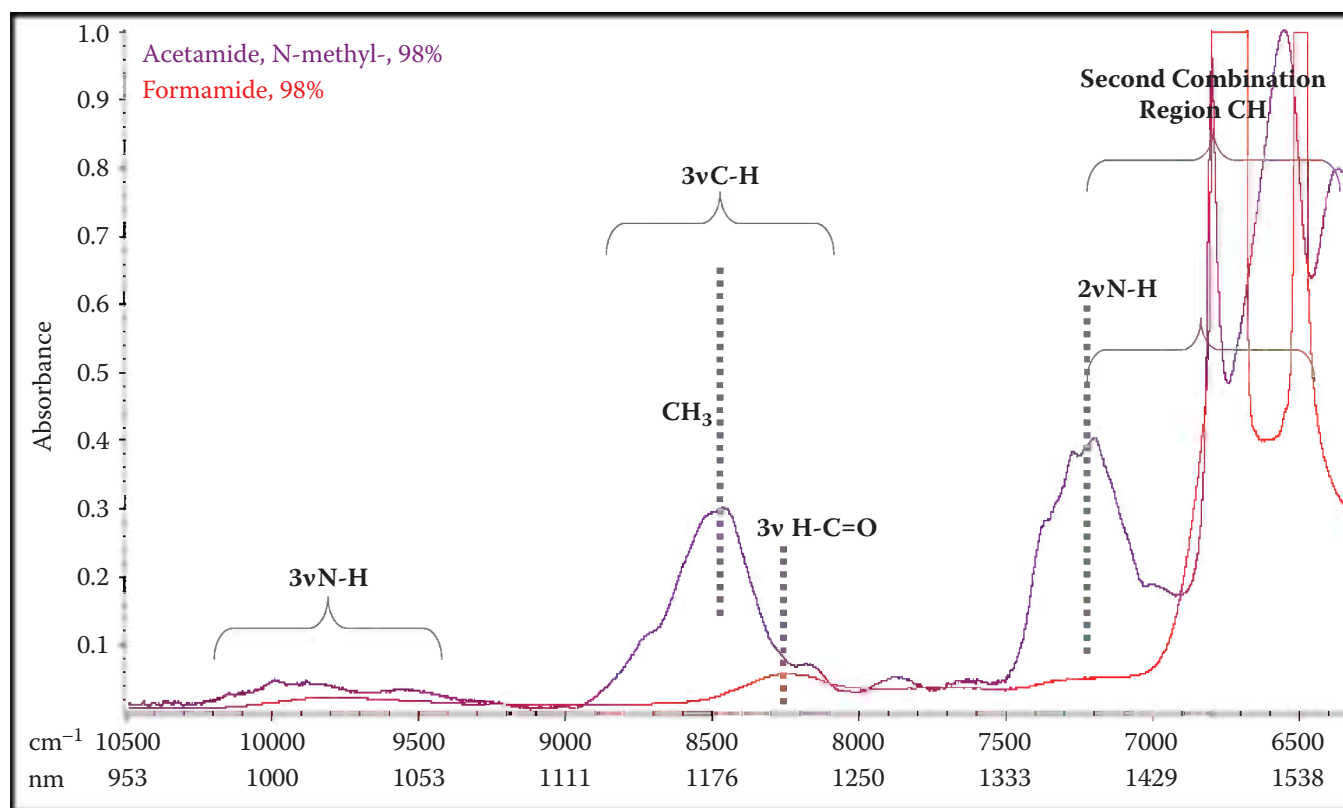
## Alkynes



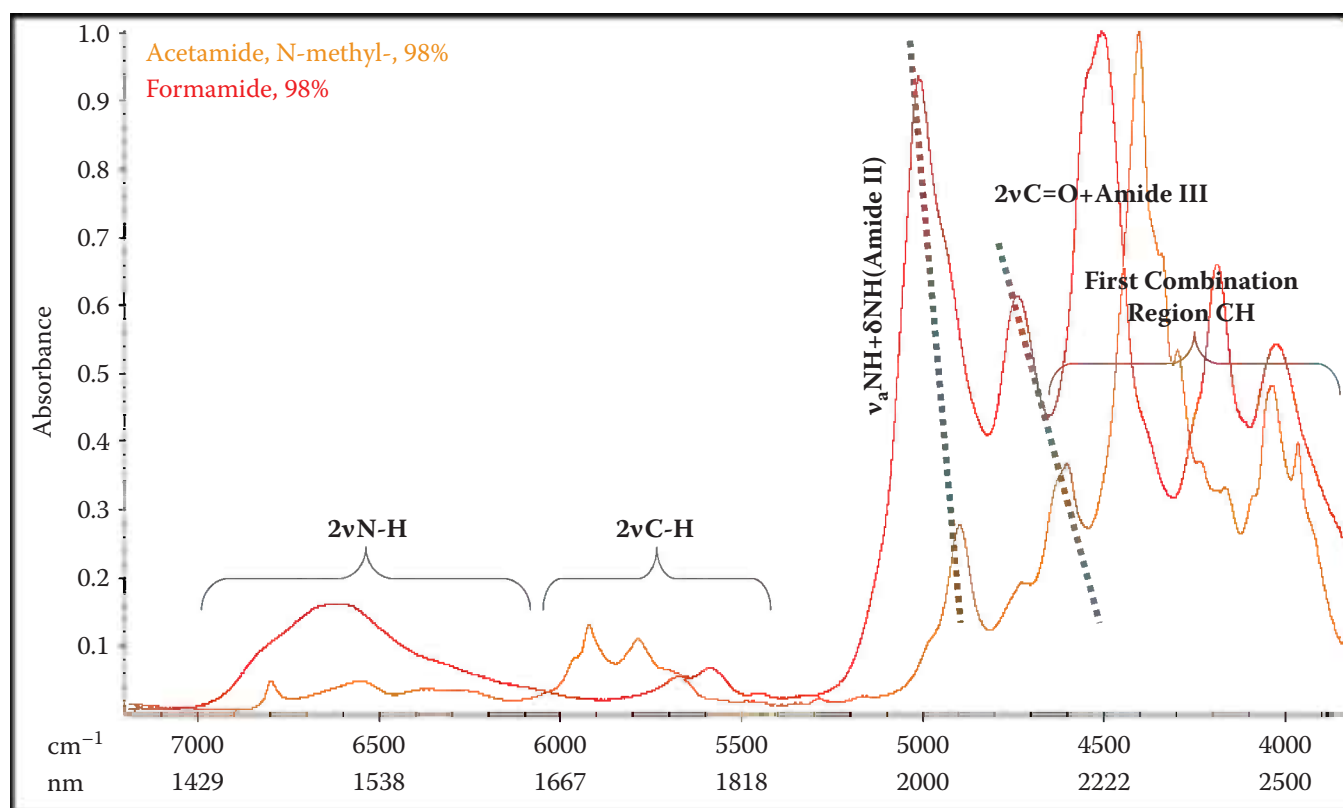
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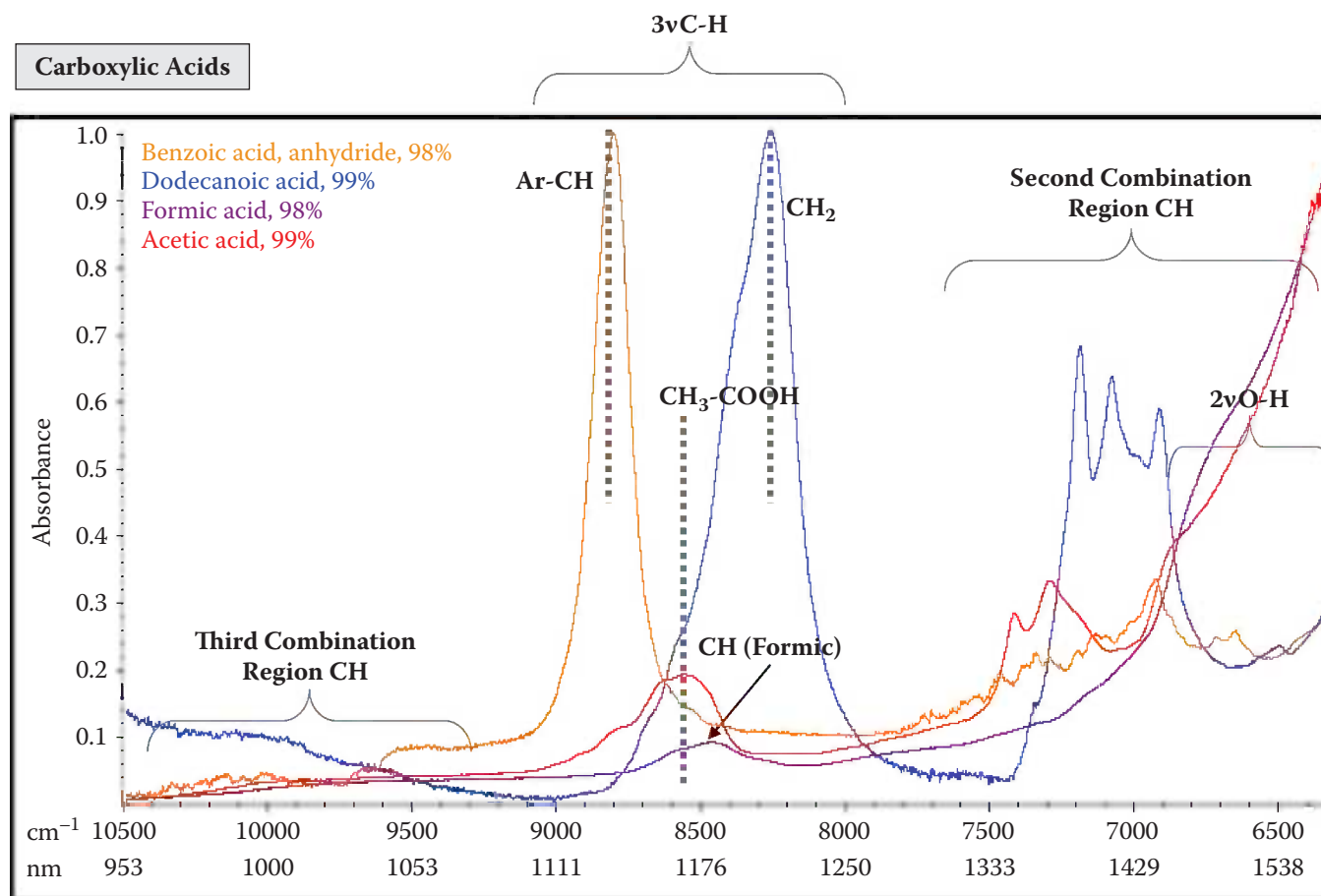


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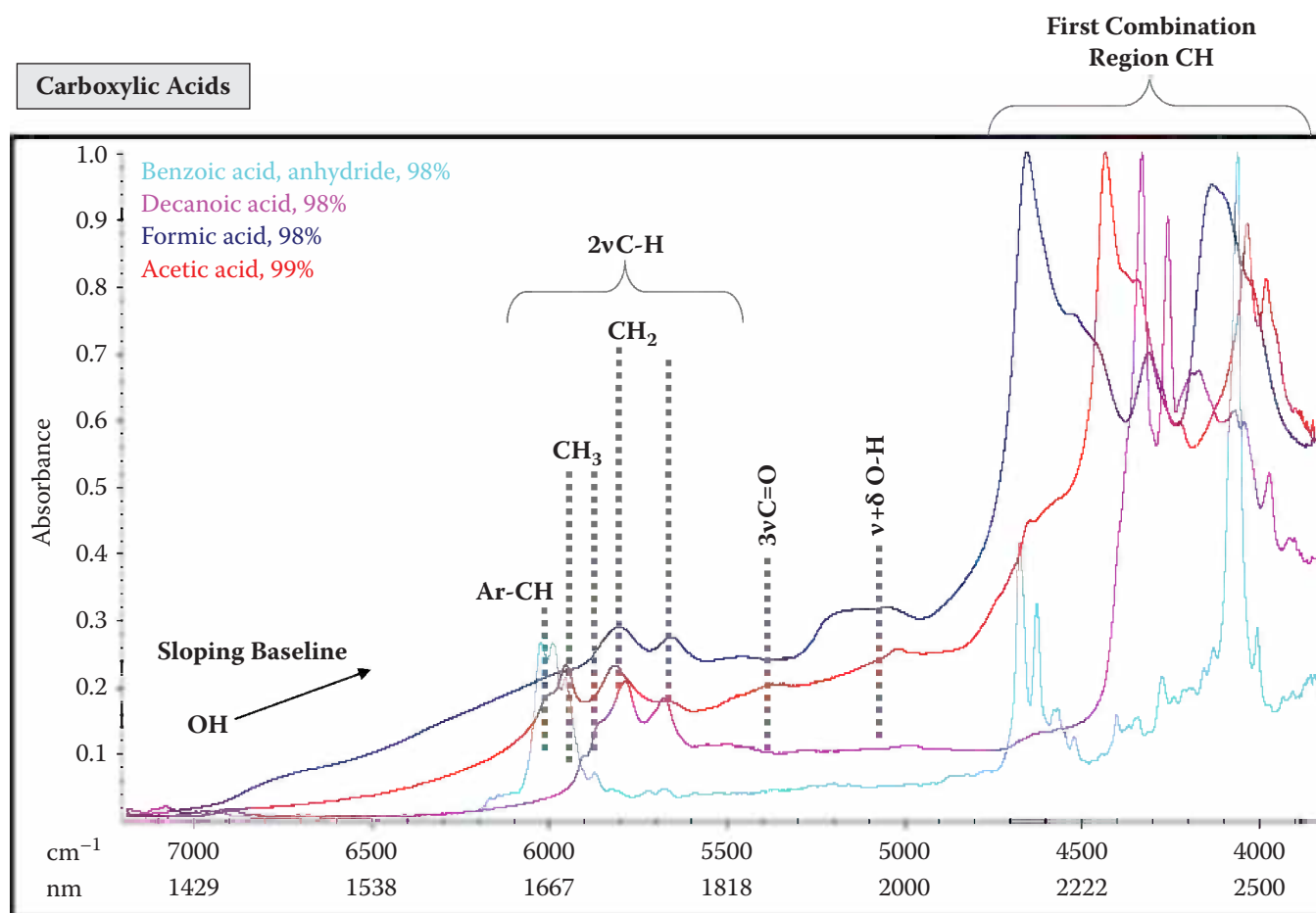


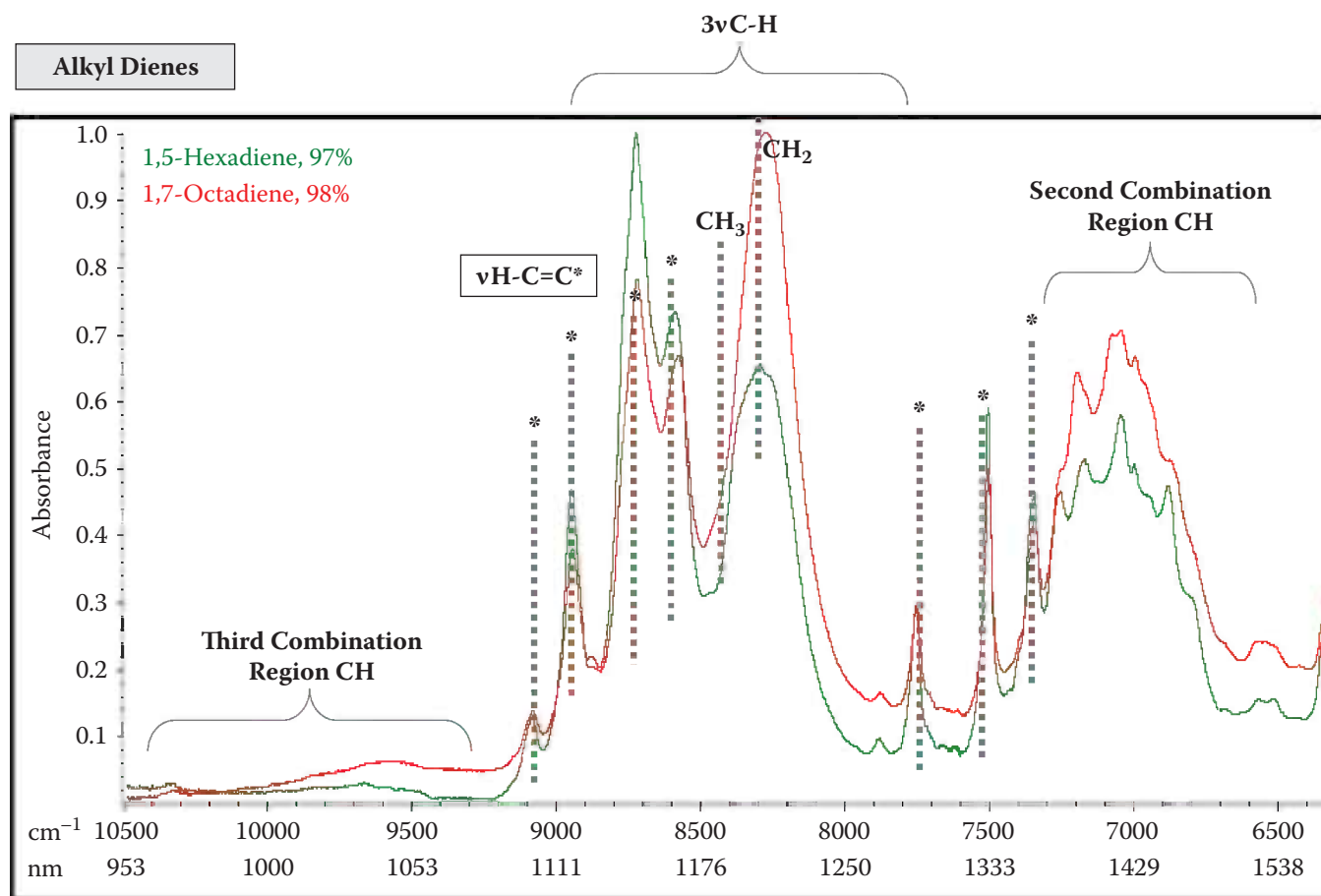
## Amides



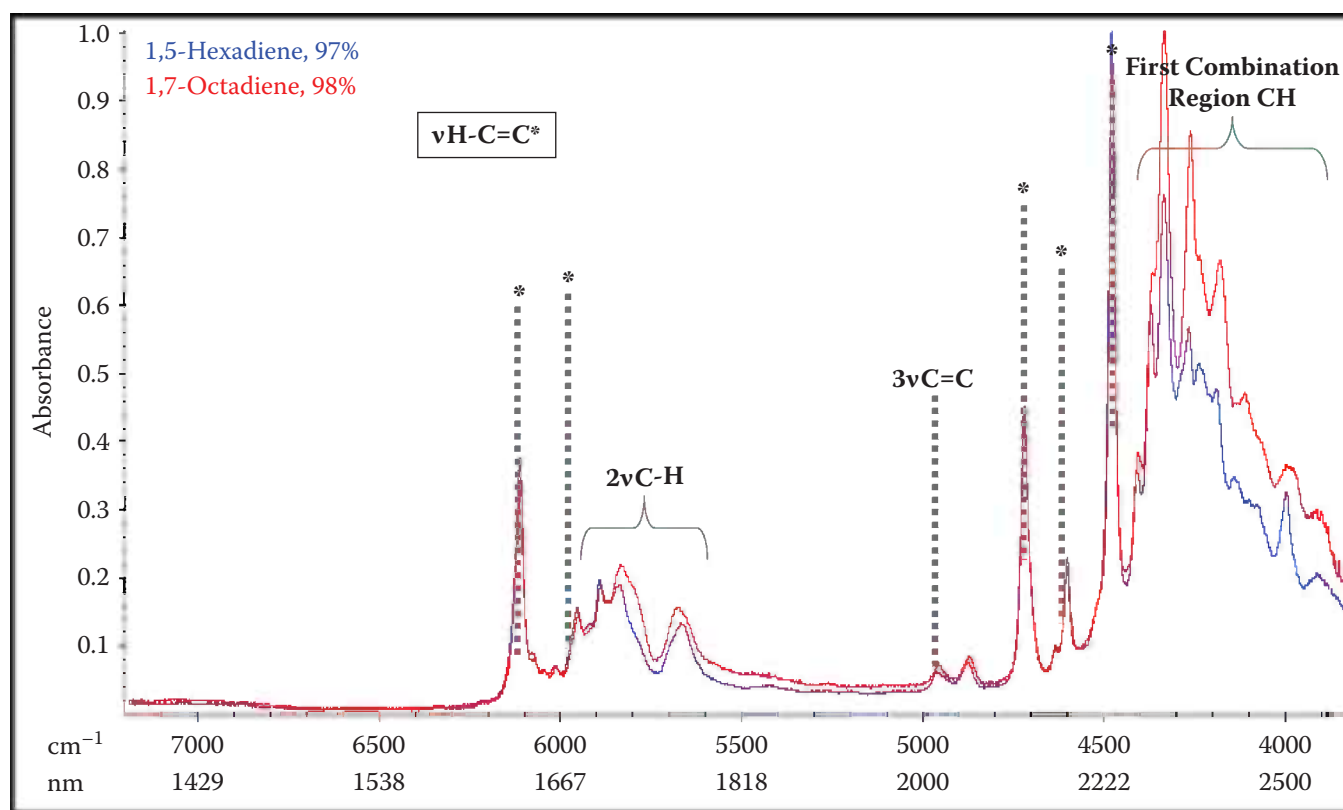


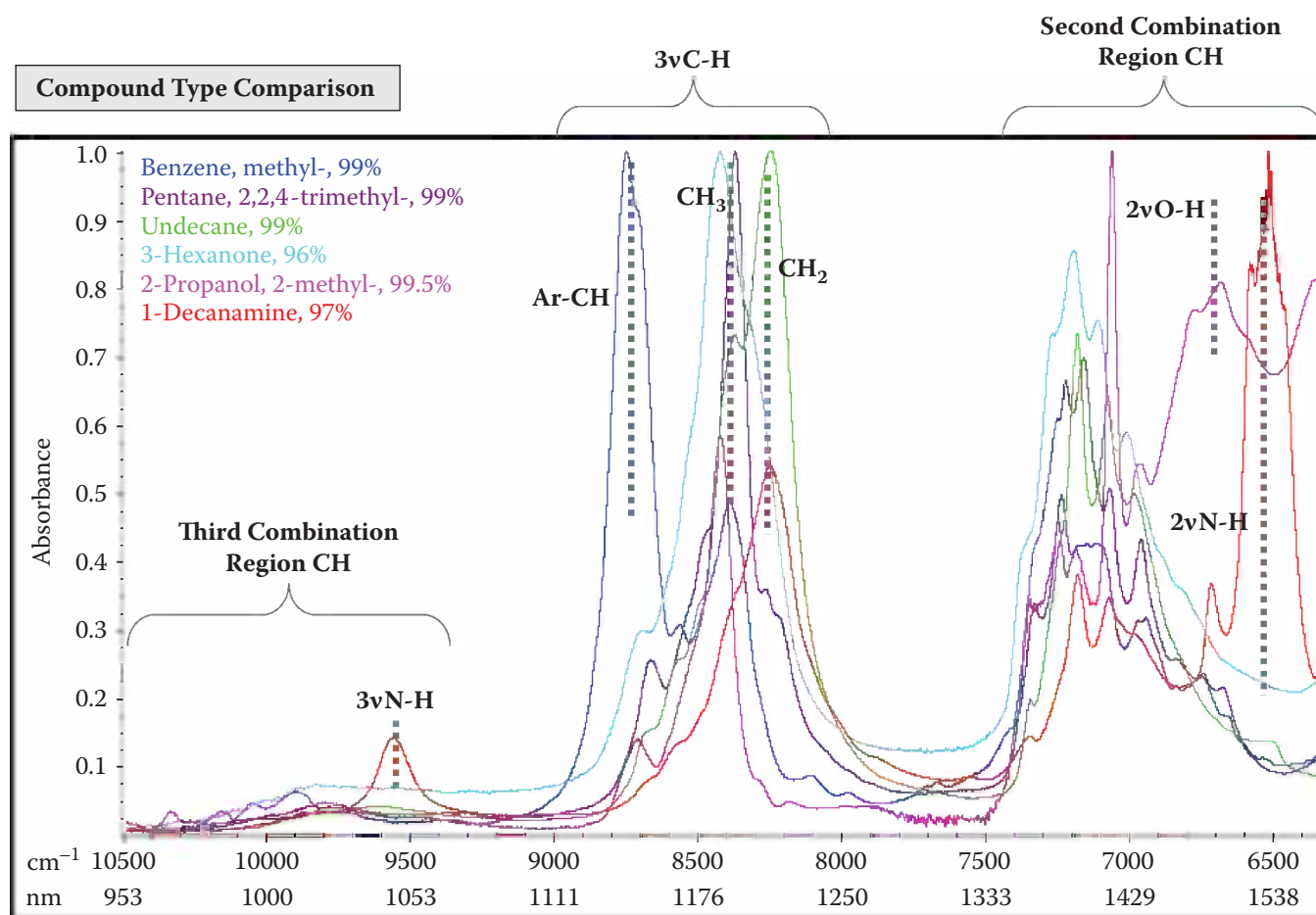


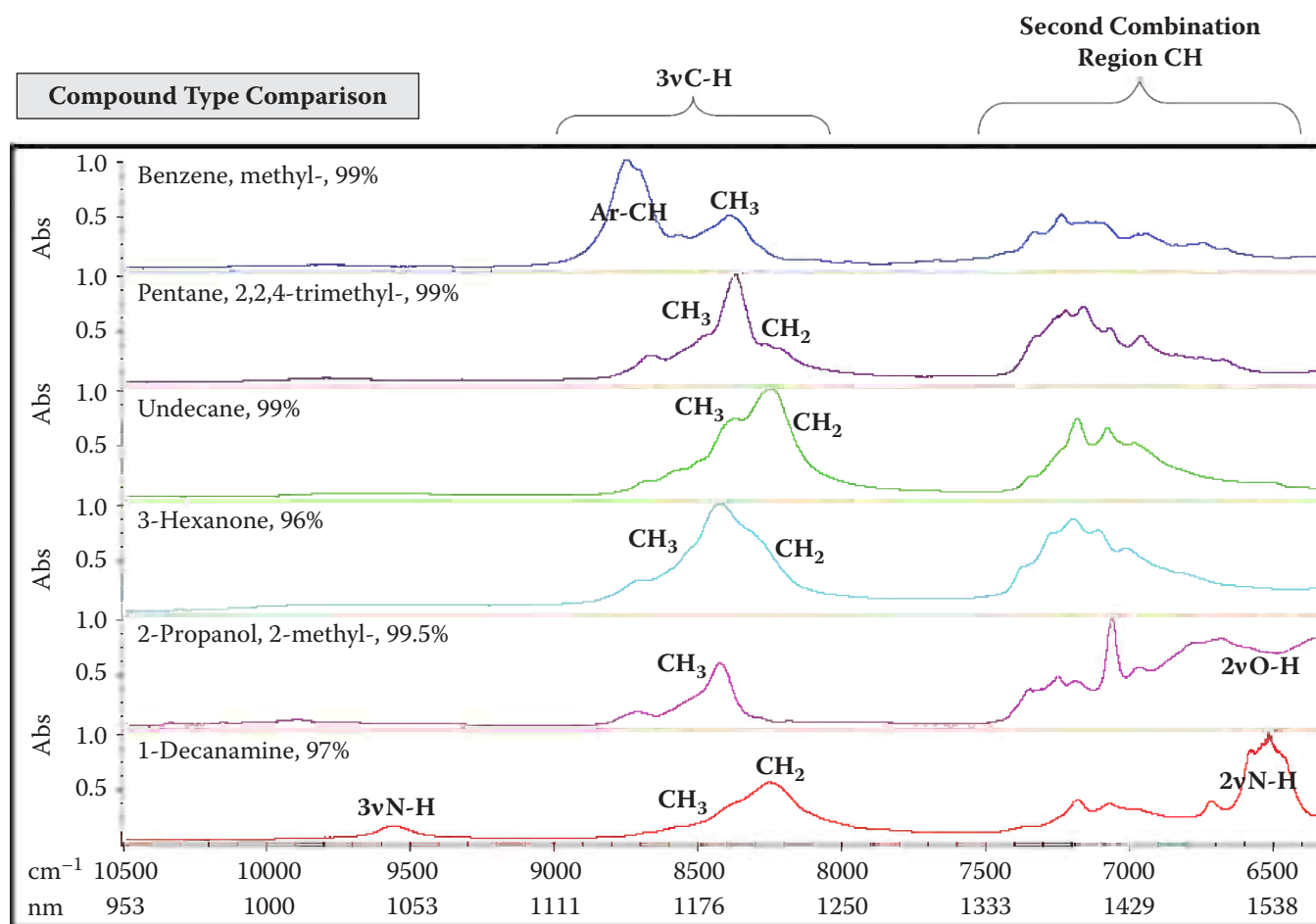




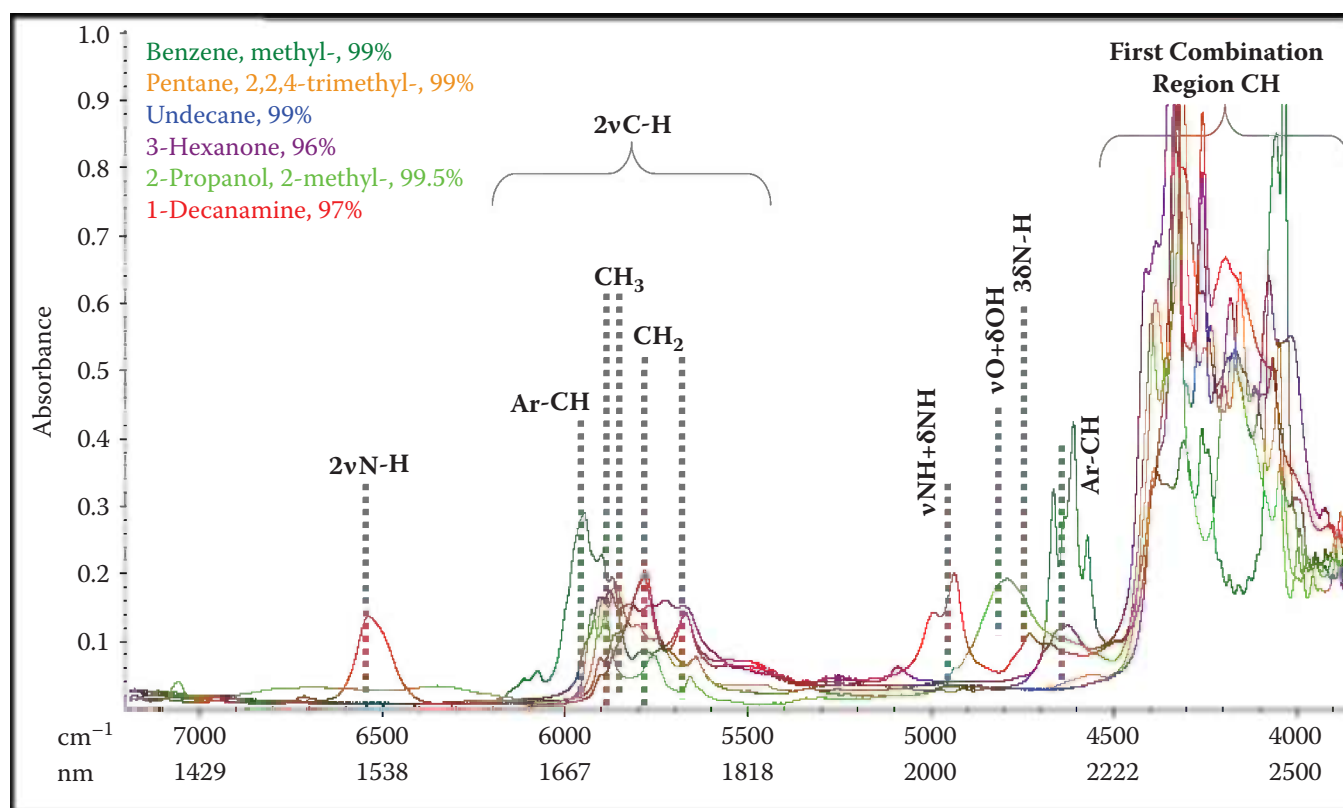
## Alkyl Dienes

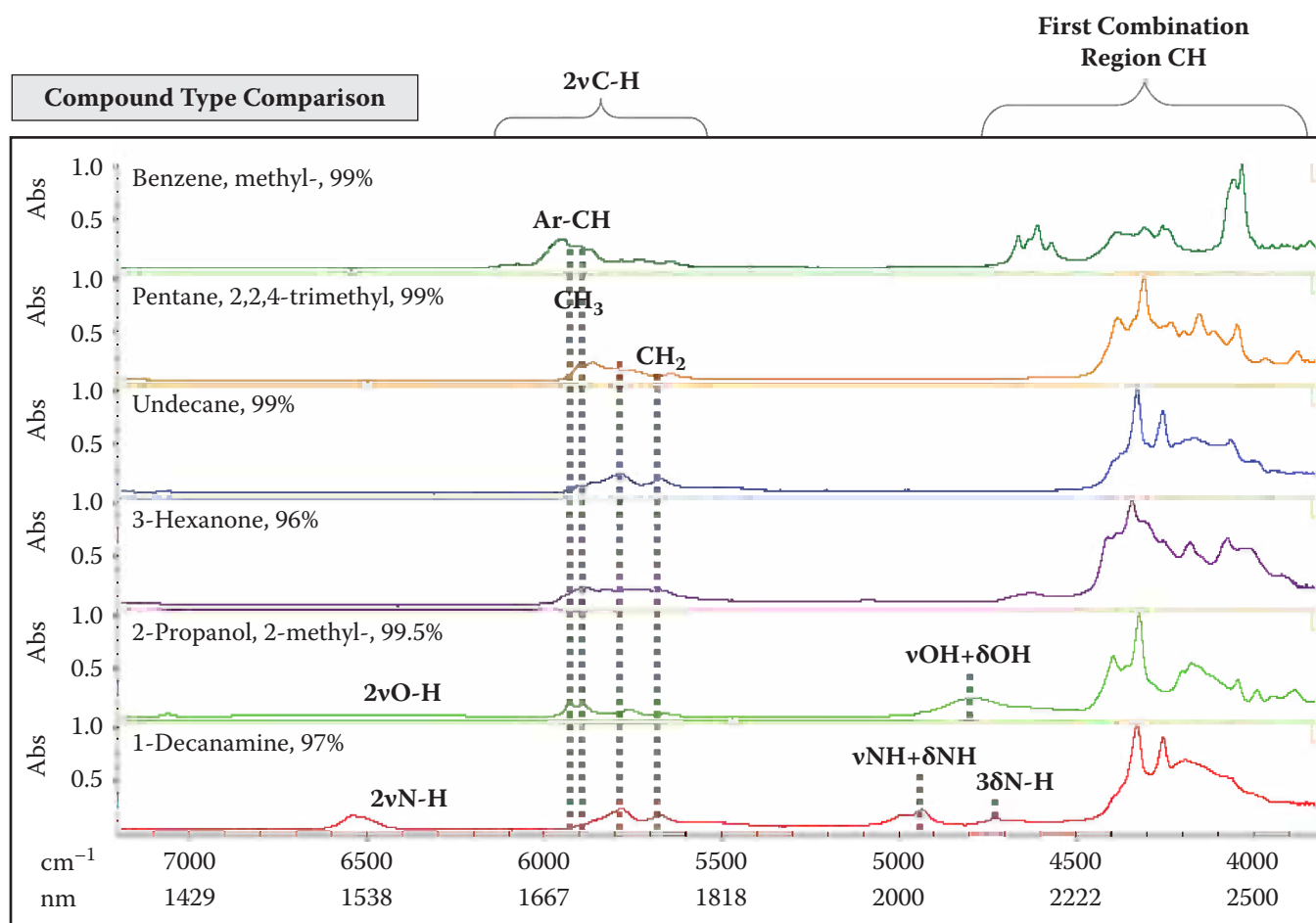


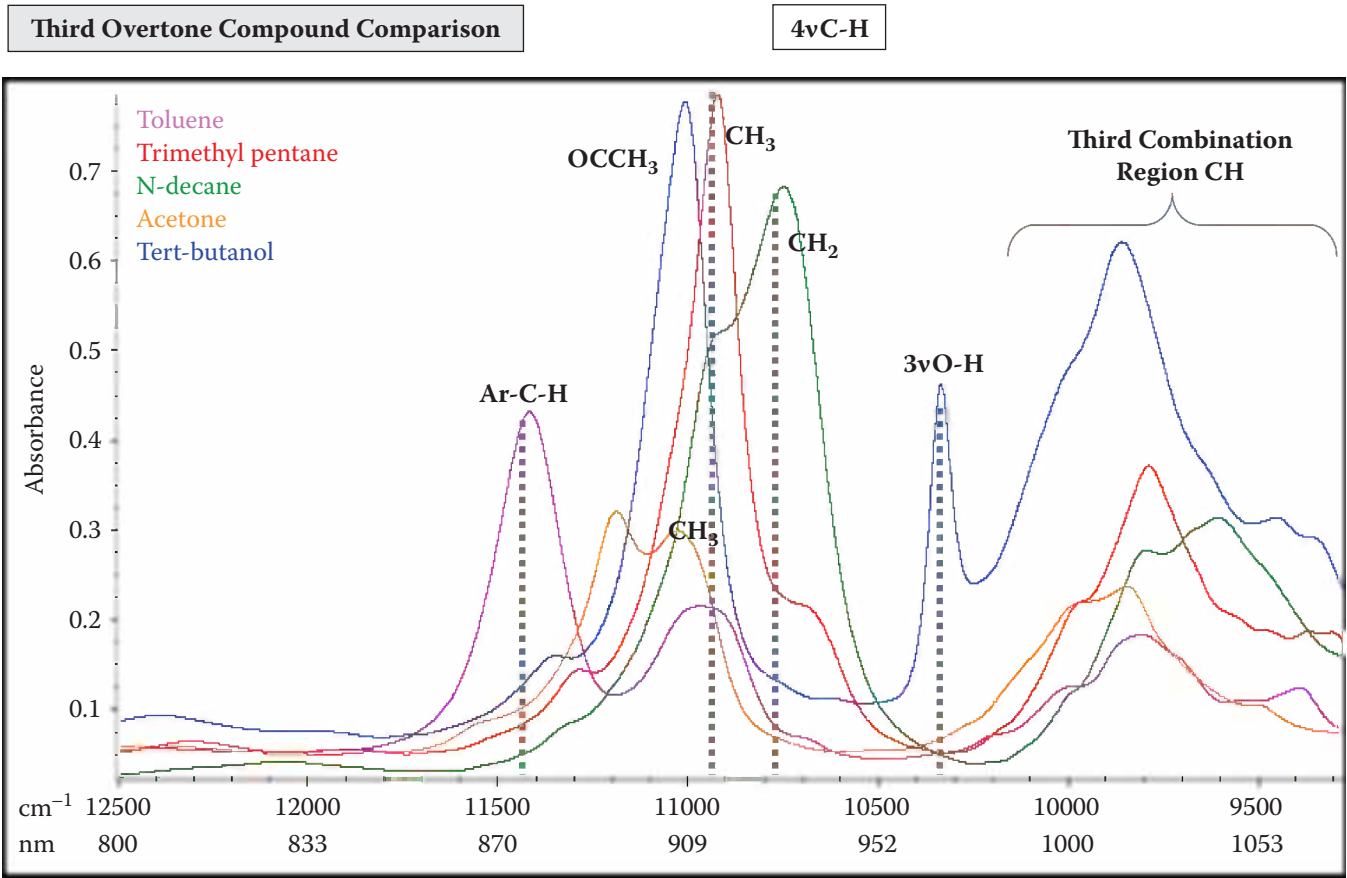




## Compound Type Comparison









# **Appendix D**

## **Spectra–Structure Correlations for Near Infrared**



| In Ascending Wavelength and Descending Wavenumber Order |                                 |   |   |                         |
|---|---------------------------------|---|---|-------------------------|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type           |
| 513   | 19500                           | O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>  | O-H (6ν) from nonhydrogen bonded short-chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH) | Alkyl alcohols          |
| 599   | 16700                           | O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>  | O-H (5ν) from nonhydrogen bonded short-chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH) | Alkyl alcohols          |
| 714   | 13986                           | C-H Aromatic (ArCH)   | C-H (5ν), Aromatic C-H  | Hydrocarbons, aromatic  |
| 741   | 13500                           | O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>  | O-H (4ν) from nonhydrogen bonded short-chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH) | Alkyl alcohols          |
| 747   | 13387                           | C-H Methyl C-H, (.CH <sub>3</sub> )   | C-H (5ν), Methyl C-H  | Hydrocarbons, aliphatic |
| 755   | 13250                           | O-H phenols, dilute phenol in CCl <sub>4</sub>  | 4νO-H dilute phenol in CCl <sub>4</sub>   | Phenolic O-H            |
| 762   | 13123                           | C-H Methylene (.CH <sub>2</sub> )   | C-H (5ν), Methylene C-H   | Hydrocarbons, aliphatic |
| 764   | 13400 and 12788 (doublet)       | O-H phenols, dilute phenol in CCl <sub>4</sub>  | 4νO-H, ortho-iodophenol   | Phenolic O-H            |
| 767   | 13038                           | O-H from primary alcohols as (-CH <sub>2</sub> -OH)   | O-H (4ν) (-CH <sub>2</sub> -OH), Primary alcohols   | primary alcohols        |
| 770   | 13000                           | O-H from Water at near 0°C  | O-H (4ν) — 3 ν <sub>1</sub> + ν <sub>3</sub>  | Water                   |
| 773   | 12937                           | O-H from secondary alcohols as (-CH-OH)   | O-H (4ν) (-CH-OH), Secondary alcohols   | Secondary alcohols      |
| 776   | 12887                           | O-H from tertiary alcohols as (-C-OH)   | O-H (4ν) (-C-OH), Tertiary alcohols   | Tertiary alcohols       |
| 796   | 12563                           | C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>              | C-H (4νCH <sub>3</sub> & δCH <sub>3</sub> ) combination                                     | Hydrocarbons, aliphatic |
| 803   | 12453                           | C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )   | C-H (4νCH <sub>3</sub> & δCH <sub>3</sub> ) combination                                     | Hydrocarbons, aromatic  |
| 813   | 12300                           | C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub>    | C-H (4νCH <sub>3</sub> & δCH <sub>3</sub> ) combination                                     | Hydrocarbons, aliphatic |
| 830   | 12048                           | C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>N</sub> R  | C-H (4νCH <sub>2</sub> & δCH <sub>2</sub> ) combination                                     | Hydrocarbons, aliphatic |
| 836   | 11962                           | C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | C-H (4νCH <sub>2</sub> & δCH <sub>2</sub> ) combination                                     | Hydrocarbons, aliphatic |
| 876   | 11655                           | C-H Aromatic (ArCH)   | C-H (4ν), Aromatic C-H  | Hydrocarbons, aromatic  |
| 908   | 11052                           | C-H Methyl (.CH <sub>3</sub> )  | C-H (4ν), .CH <sub>3</sub>  | Hydrocarbons, methyl    |
| 915   | 10929                           | C-H Methyl C-H, (.CH <sub>3</sub> )   | C-H (4ν), Methyl C-H  | Hydrocarbons, aliphatic |
| 930   | 10753                           | C-H Methylene (.CH <sub>2</sub> )   | C-H (4ν), Methylene C-H   | Hydrocarbons, aliphatic |
| 930   | 10800                           | C-H Methylene (.CH <sub>2</sub> )   | C-H (4ν), .CH <sub>2</sub>  | Hydrocarbons, methylene |
| 962   | 10400                           | O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>  | O-H (3ν) from nonhydrogen bonded short chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH) | Alkyl alcohols          |
| 979   | 10210                           | O-H from Water at near 0°C  | O-H (3ν) — 2 ν <sub>1</sub> + ν <sub>3</sub>  | Water                   |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |   |  |
|---|---------------------------------|--|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure   | Material Type                              |
| 990   | 9911 and 10288 (doublet)        | O-H phenols, dilute phenol in CCl <sub>4</sub>   | 3νO-H, ortho-iodophenol   | Phenolic O-H                               |
| 996   | 10040                           | O-H from primary alcohols as (-CH <sub>2</sub> -OH)  | O-H (3ν) (-CH <sub>2</sub> -OH), Primary alcohols   | Primary alcohols                           |
| 1000  | 10,000                          | O-H phenols, dilute phenol in CCl <sub>4</sub>   | 3νO-H dilute phenol in CCl <sub>4</sub>   | Phenolic O-H                               |
| 1003.0  | 9970                            | N-H primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent  | Aromatic amine                             |
| 1004  | 9960                            | O-H from secondary alcohols as (-CH-OH)  | O-H (3ν) (-CH-OH), Secondary alcohols   | Secondary alcohols                         |
| 1006  | 9940                            | O-H from tertiary alcohols as (-C-OH)  | O-H (3ν) (-C-OH), Tertiary alcohols   | Tertiary alcohols                          |
| 1015.0  | 9852                            | N-H primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent   | Aromatic amine                             |
| 1017.5  | 9828                            | N-H primary aromatic amine ( <i>o</i> -Cl)   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping                  | Aromatic amine                             |
| 1018.5  | 9818                            | N-H primary aromatic amine ( <i>m</i> -Cl)   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent                | Aromatic amine                             |
| 1018.5  | 9818                            | N-H primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> )  | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent | Aromatic amine                             |
| 1019.0  | 9813                            | N-H primary aromatic amine ( <i>p</i> -Cl)   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                | Aromatic amine                             |
| 1021  | 9796                            | C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | C-H (3νCH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, Aromatic                     |
| 1021  | 9794                            | C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | C-H (3νCH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, aliphatic                    |
| 1021  | 9795                            | C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>           | C-H (3νCH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, aliphatic                    |
| 1021.0  | 9794                            | N-H primary aromatic amine (no other substituents)   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                 | Aromatic amine                             |
| 1023.0  | 9775                            | N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping      | Aromatic amine                             |
| 1026.5  | 9741                            | N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )   | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping      | Aromatic amine                             |
| 1029  | 9720                            | O-H/C-O Polyfunctional alkyl alcohols  | 2ν O-H & 3νC-O combination  | Ethers and esters also containing alcohols |
| (continued)   |                                 |  |   |  |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |  |
|---|---------------------------------|---|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type                          |
| 1041  | 9606                            | C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>N</sub> R  | C-H (3νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| 1042  | 9600                            | C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | C-H (3νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| 1047  | 9550                            | O-H with hydrogen bonding (R-C-OH)  | O-H (3ν) from hydrogen bonded short chain alkyl compounds   | Alkyl alcohols                         |
| 1065  | 9386                            | O-H combination band, alcohols or water   | 2νO-H & δ C-H methyl combination  | Alcohols as R-C-O-H                    |
| 1142  | 8754                            | C-H Aromatic (ArCH)   | C-H (3ν), Aromatic C-H  | Hydrocarbons, aromatic                 |
| 1143  | 8749                            | C-H (Aromatic C-H)  | C-H (3ν), Ar.C-H  | Hydrocarbons, aromatic                 |
| 1160  | 8621                            | C=O (Carbonyl >C=O)   | C=O (5ν)  | Hydrocarbons, aliphatic                |
| 1170  | 8547                            | C-H Alkene (.HC=CH)   | C-H (3ν), .HC=CH  | Alkenes, polyenes                      |
| 1194  | 8375                            | C-H Methyl C-H, (.CH <sub>3</sub> )   | C-H (3ν), Methyl C-H  | Hydrocarbons, aliphatic                |
| 1195  | 8368                            | C-H Methyl (.CH <sub>3</sub> )  | C-H (3ν), .C-H <sub>3</sub>   | Hydrocarbons, aliphatic                |
| 1200  | 8310                            | O-H from Water at near 0°C  | O-H, .O-H — ν <sub>1</sub> + ν <sub>2</sub> + ν <sub>3</sub>  | Water                                  |
| 1211  | 8258                            | C-H Methylene (.CH <sub>2</sub> )   | C-H (3ν), Methylene C-H   | Hydrocarbons, aliphatic                |
| 1215  | 8230                            | C-H Methylene (.CH <sub>2</sub> )   | C-H (3ν), .C-H <sub>2</sub>   | Hydrocarbons, aliphatic                |
| 1225  | 8163                            | C-H Secondary or Tertiary Carbon (.CH)  | C-H (3ν), .C-H  | Hydrocarbons, aliphatic                |
| 1360  | 7353                            | C-H Methyl (.CH <sub>3</sub> )  | C-H combination, .C-H <sub>3</sub>  | Hydrocarbons, Aliphatic                |
| 1370  | 7300                            | C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )   | C-H (2νCH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, aromatic                 |
| 1390  | 7194                            | C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>              | C-H (2ν <sub>s</sub> CH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, aliphatic                |
| 1395  | 7168                            | C-H Methylene (.CH <sub>2</sub> )   | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic                |
| 1396  | 7163                            | C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub>    | C-H (2νCH <sub>3</sub> & δCH <sub>3</sub> ) combination   | Hydrocarbons, aliphatic                |
| 1408  | 7100                            | O-H Methanol O-H with hydrogen bonding  | O-H (2ν) from non-hydrogen bonded methanol in CCl <sub>4</sub> as (CH <sub>3</sub> -OH)   | O-H from Methanol (nonhydrogen bonded) |
| 1410  | 7092                            | C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>N</sub> R  | C-H (2νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| 1410  | 7092                            | O-H Alcohol (RO-H)  | O-H (2ν), .O-H  | Hydrocarbons, aliphatic                |
| 1410  | 7090                            | O-H Hydroxyl O-H free form (not hydrogen bonded)  | O-H, free hydroxyl group in dilute CCl <sub>4</sub>   | O-H not hydrogen bonded                |
| 1410  | 7120–7030                       | O-H from alcohols in CCl <sub>4</sub> ; first overtone (2 ν <sub>s</sub> ) of the O-H alcoholic stretching modes              | O-H from alcohols in CCl <sub>4</sub> as n-, sec-, and tert-butanol; the three kinds of alcohols showed an intense band due to the first overtone (2ν) of the OH stretching modes | Alcohols in CCl <sub>4</sub>           |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |                                     |
|---|---------------------------------|---|---|-------------------------------------|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type                       |
| 1411  | 7085                            | C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | C-H (2νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic             |
| 1415  | 7067                            | C-H Methylene (.CH <sub>2</sub> )   | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic             |
| 1415  | 7065                            | O-H Alcoholic O-H, non-hydrogen bonded  | O-H (2ν) non-bonded from diols  | Alkyl alcohols (diols)              |
| 1416  | (7060 primarily)<br>7200–7015   | O-H Alcohol O-H with hydrogen bonding   | O-H (2ν) from butanol   | Alkyl alcohols (containing one O-H) |
| 1417  | 7057                            | C-H Aromatic C-H  | C-H combination, Ar.C-H   | Hydrocarbons, aromatic              |
| 1420  | 7042                            | O-H Aromatic (ArO-H)  | O-H (2ν), .O-H  | Hydrocarbons, aromatic              |
| 1420  | 7040                            | O-H, Monomeric phenol in CCl <sub>4</sub>   | 2ν O-H monomeric phenol in CCl <sub>4</sub>   |                                     |
| 1420  | 7140–6940                       | O-H Phenolic O-H  | 2νO-H from phenols and aryl alcohols Ar-OH  | Phenolic O-H                        |
| 1430  | 6995                            | N-H from primary amides (R-C=O – NH <sub>2</sub> )  | N-H (2ν) symmetric from primary amide (R-C=O – NH <sub>2</sub> )                                      | N-H from primary amides             |
| 1432.0  | 6982                            | N-H primary aromatic amine (o-NO <sub>2</sub> )   | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent  | Aromatic amine                      |
| 1440  | 6944                            | C-H Methylene (.CH <sub>2</sub> )   | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic             |
| 1441.0  | 6940                            | N-H primary aromatic amine (m-NO <sub>2</sub> )   | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent   | Aromatic amine                      |
| 1441  | 6940                            | O-H from sugar as crystalline sucrose   | O-H (2ν) carbohydrates (C4 hydroxyl within a crystalline matrix)                                      | Crystalline sucrose                 |
| 1443.0  | 6930                            | N-H primary aromatic amine (o-Cl)   | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping                  | Aromatic amine                      |
| 1445.0  | 6920                            | N-H primary aromatic amine (m-Cl)   | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent                | Aromatic amine                      |
| 1446  | 6916                            | C-H Aromatic (ArC-H)  | C-H combination, ArC-H  | Hydrocarbons, aromatic              |
| 1446.0  | 6916                            | N-H primary aromatic amine (o—OCH <sub>3</sub> )  | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent | Aromatic amine                      |
| 1448.0  | 6906                            | N-H primary aromatic amine (p-Cl)   | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                | Aromatic amine                      |
| 1448.5  | 6904                            | N-H primary aromatic amine (no other substituents)  | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                 | Aromatic amine                      |
| (continued)   |                                 |   |   |                                     |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |  |  |
|---|---------------------------------|--|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure  | Material Type                            |
| 1450  | 6897                            | C=O (Carbonyl >C=O)  | C=O (4v)   | Ketones & aldehydes                      |
| 1450  | 6897                            | O-H Polymeric (.O-H)   | O-H (2v), .O-H   | Starch/Polymeric alcohol                 |
| 1452  | 6887                            | O-H from primary alcohols as (-CH <sub>2</sub> -OH) and H <sub>2</sub> O | O-H (2v) (-CH <sub>2</sub> -OH), Primary alcohols and H <sub>2</sub> O   | Primary alcohols (H <sub>2</sub> O)      |
| 1452  | 6887                            | Si-O from silicone   | Si-O (2v) stretch from silicone (dimethyl siloxane)  | Si-O from silicone (dimethyl siloxane)   |
| 1452.5  | 6885                            | N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )                 | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping                       | Aromatic amine                           |
| 1453  | 6880                            | O-H from Water at near 0°C   | O-H (2v), .O-H   | Water                                    |
| 1459.5  | 6852                            | N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )                 | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping                       | Aromatic amine                           |
| 1460  | 6849                            | N-H Amide .NH or .NH <sub>2</sub>  | N-H (2v), symmetrical  | Urea                                     |
| 1460  | 6850                            | O-H Alcoholic O-H, intra-molecularly bonded                              | O-H (2v) intra-molecularly bonded from diols   | Alkyl alcohols (diols)                   |
| 1461  | 6844                            | N-H for secondary amine as (R-NH-R)                                      | N-H (2v), secondary amine as (R-NH-R), indole, first overtone band intensity comparisons, CCl <sub>4</sub> solution    | N-H secondary amine                      |
| 1463  | 6835                            | N-H Amide .NH or .NH <sub>2</sub>  | N-H (2v), .CONH <sub>2</sub>   | Amide/Protein                            |
| 1464  | 6831                            | O-H from secondary alcohols as (-CH <sub>2</sub> -OH)                    | O-H (2v) (-CH <sub>2</sub> -OH), Secondary alcohols  | Secondary alcohols                       |
| 1464  | 6830                            | O-H phenols, Ortho-substituted halogens                                  | 2vO-H in ortho-substituted halogens on phenols   | Phenolic O-H                             |
| 1465  | 6826                            | N-H for secondary amine as (R-NH-R)                                      | N-H (2v), secondary amine as (R-NH-R), Carbazole, first overtone band intensity comparisons, CCl <sub>4</sub> solution | N-H secondary amine                      |
| 1468  | 6812                            | O-H from tertiary alcohols as (-C-OH)                                    | O-H (2v) (-C-OH), Tertiary alcohols  | Tertiary alcohols                        |
| 1470  | 6803                            | N-H band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )             | N-H (2v) asymmetric stretching from urea   | N-H from urea                            |
| 1470  | 6805                            | N-H combination band from primary amides (R-C=O – NH <sub>2</sub> )      | N-H (vN-H asymmetric & vN-H symmetric combination) for primary amides  | N-H combination band from primary amides |
| 1470  | 6800                            | O-H Methanol O-H with hydrogen bonding                                   | O-H (2v) from nonhydrogen bonded methanol in CCl <sub>4</sub> as (CH <sub>3</sub> -OH)                                 | O-H from methanol (nonhydrogen bonded)   |
| 1471  | 6798                            | N-H Amide with N-R group   | N-H (2v), .CONHR   | Amide/protein                            |
| 1472  | 6791                            | N-H primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )                 | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent                    | Aromatic amine                           |
| 1480  | 6760                            | N-H nonbonded from polyamide 11  | N-H (2v) stretching nonbonded N-H from Polyamide 11  | Polyamide 11                             |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |  |                          |
|---|---------------------------------|---|--|--------------------------|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure  | Material Type            |
| 1481  | 6751                            | N-H for secondary amine as (R-NH-R)   | N-H (2v), secondary amine as (R-NH-R), N-benzylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution | N-H secondary amine      |
| 1483  | 6743                            | N-H Amide .NH or .NH <sub>2</sub>   | N-H (2v), .CONH <sub>2</sub>   | Amide/protein            |
| 1485  | 6736                            | N-H band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )  | N-H (2v) symmetric stretching from urea  | N-H from urea            |
| 1486  | 6729                            | N-H for secondary amine as (R-NH-R)   | N-H (2v), secondary amine as (R-NH-R), diphenylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution | N-H secondary amine      |
| 1487.0  | 6725                            | N-H primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent                         | Aromatic amine           |
| 1489.5  | 6713                            | N-H primary aromatic amine ( <i>m</i> -Cl)  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent                                      | Aromatic amine           |
| 1490  | 6711                            | N-H Amide with N-R group  | N-H (2v), .CONHR   | Amide/Protein            |
| 1490  | 6710                            | N-H from primary amides (R-C=O – NH <sub>2</sub> )  | N-H (2v) asymmetric from primary amide (R-C=O – NH <sub>2</sub> )  | N-H from primary amides  |
| 1490  | 6711                            | O-H Polymeric (.O-H)  | O-H (2v), .O-H   | Starch/Polymeric alcohol |
| 1491.5  | 6705                            | N-H primary aromatic amine ( <i>o</i> -Cl)  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping  | Aromatic amine           |
| 1491.5  | 6705                            | N-H primary aromatic amine ( <i>p</i> -Cl)  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                                      | Aromatic amine           |
| 1492  | 6702                            | N-H Amide .NH or .NH <sub>2</sub>   | N-H (2v), ArNH <sub>2</sub>  | Amide/protein            |
| 1492.5  | 6700                            | N-H primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> )   | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent                       | Aromatic amine           |
| 1493  | 6698                            | N-H from primary and secondary aromatic amine (mixtures of aniline and N-ethylaniline in CCl <sub>4</sub> ) | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent                       | Aromatic amines          |
| 1493.0  | 6698                            | N-H primary aromatic amine (no other substituents)  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                                       | Aromatic amine           |
| 1496.5  | 6683                            | N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )  | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping                            | Aromatic amine           |
| 1500  | 7100–6240                       | O-H stretching band, alcohols or water  | 2vO-H of different aggregates, such as monomers, dimers, and polyols   | Alcohols or water O-H    |
| 1500  | 6667                            | N-H Amide .NH or .NH <sub>2</sub>   | N-H (2v), .NH <sub>2</sub>   | Amide/protein            |

(continued)



| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |  |  |
|---|---------------------------------|--|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure  | Material Type                                    |
| 1500  | 6666                            | N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )                         | N-H (νN-H asymmetric & νN-H symmetric combination) from urea   | N-H from urea                                    |
| 1500  | 6850–6240                       | O-H Alcohol O-H with hydrogen bonding  | O-H (2ν) from hydrogen bonded alkyl alcohols as (R-C-OH)   | Alkyl alcohols (containing one O-H)              |
| 1502.5  | 6656                            | N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )   | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping                                    | Aromatic amine                                   |
| 1510  | 6623                            | N-H Amide .NH or .NH <sub>2</sub>  | N-H (2ν), .CONH <sub>2</sub>   | Amide/protein                                    |
| 1515  | 6600                            | N-H bonded from polyamide 11   | N-H (2ν) stretching bonded NH, disordered phase from polyamide 11  | Polyamide 11                                     |
| 1520  | 6579                            | N-H Amide .NH or .NH <sub>2</sub>  | N-H (2ν), .CONH <sub>2</sub>   | Amide/protein                                    |
| 1520  | 6580                            | N-H for secondary amine as (R-NH-R)  | N-H (2ν), secondary amine as (R-NH-R), Dimethylamine (vapor), first overtone band intensity comparisons, CCl <sub>4</sub> solution | N-H secondary amine                              |
| 1530  | 6536                            | C-H Alkyne C-H as (R-C-C≡C-H)  | C-H, Alkyne (1-hexyne) as (R-C-C≡C-H)  | Acetylene or Alkyne C-H                          |
| 1530  | 6536                            | N-H Amide .NH or .NH <sub>2</sub>  | N-H (2ν), RNH <sub>2</sub>   | Amide/protein                                    |
| 1530  | 6536                            | N-H for secondary amine as (R-NH-R)  | N-H (2ν), secondary amine as (R-NH-R), morpholine, first overtone band intensity comparisons, CCl <sub>4</sub> solution            | N-H secondary amine                              |
| 1534  | 6250                            | N-H ammonia in water   | N-H (2ν) for NH <sub>3</sub> (ammonia) in water  | Ammonia in water                                 |
| 1538  | 6500                            | N-H bonded from polyamide 11   | N-H (2ν) stretching bonded NH, ordered phase from polyamide 11   | Polyamide 11                                     |
| 1540  | 6494                            | O-H Polymeric (.O-H)   | O-H (2ν), .O-H   | Starch/polymeric alcohol                         |
| 1545  | 6471                            | N-H for secondary amine as (R-NH-R)  | N-H (2ν), secondary amine as (R-NH-R), diethylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution          | N-H secondary amine                              |
| 1550  | 6450                            | O-H bound water and the first overtone of an NH stretching mode of the amide groups of ovalbumin | O-H bound water with several hydrogen bonds and the first overtone of an NH stretching mode of the amide groups of ovalbumin       | O-H bound water of the amide groups of ovalbumin |
| 1550  | 6540–6250                       | N-H from secondary amide in proteins   | N-H (2ν) stretching from secondary amide in proteins   | N-H from protein                                 |
| 1570  | 6369                            | N-H Amide .NH  | N-H (2ν), .CONHR   | Amide/protein                                    |
| 1570  | 6368                            | N-H bonded combination from Polyamide 11   | N-H [Bonded NH stretching & 2x Amide II deformation (N-H in-plane bending) combination] from polyamide 11                          | Polyamide 11                                     |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |   |  |
|---|---------------------------------|--|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure   | Material Type  |
| 1580  | 6330                            | O-H combination band, alcohols or water  | 2νO-H , O-H broad band, hydrogen bonded   | Alcohols as R-C-O-H  |
| 1583  | 6319                            | O-H stretching band, alkyl alcohols or water   | νO-H & δO-H combination reported in the literature from ethylene-vinyl alcohol copolymer spectra, probably better assigned as 2νO-H | Alcohols or water O-H  |
| 1598  | 6256                            | C=O/N-H combination from polyamide 11  | C=O/N-H [Amide I (2ν <sub>S</sub> C=O stretching) & 3 x Amide II (N-H in-plane bending) combination] from polyamide 11              | Polyamide 11   |
| 1613  | 6200                            | C-H Vinyl C-H attached to >C=O group, such as (CH <sub>2</sub> =CH-C=O - )                 | C-H, Vinyl on O (1-ethenyloxybutane) as (CH <sub>2</sub> =CH-C=O - )  | Vinyl as 1-ethenyl oxybutane (1-ethenyl- methyl-ethyl-ketone)  |
| 1618  | 6180                            | N-H from Polyamide 11  | N-H [4 x Amide II (N-H in-plane bending)] from Polyamide 11   | Polyamide 11   |
| 1620  | 6173                            | C-H Alkene, =CH <sub>2</sub>   | C-H (2ν), =CH <sub>2</sub>  | Alkenes  |
| 1621  | 6169                            | C-H Acrylate C-H as (CH <sub>2</sub> =CHCOO <sup>-</sup> )                                 | C- H, combination of two stretching modes   | Acrylate   |
| 1621  | 6170                            | C-H Vinyl C-H attached to N group, such as (CH <sub>2</sub> =CH-N-C=O – C)                 | C-H, Vinyl on N (1-ethenyl 2-pyrrolidinone) as (CH <sub>2</sub> =CH-N-C=O – C)  | Vinyl on pyrrolidinone   |
| 1630  | 6130/6140                       | C-H Vinyl and vinylidene C-H as (CH <sub>2</sub> =C(CH <sub>3</sub> )–CH=CH <sub>2</sub> ) | C-H, Vinyl and vinylidene (2-methyl–1,3-butadiene), isoprene as (CH <sub>2</sub> =C(CH <sub>3</sub> )–CH=CH <sub>2</sub> )          | Vinyl and vinylidene C-H as isoprene                           |
| 1631  | 6130                            | C-H Vinylidene C-H, associated with (CH <sub>2</sub> =C<)                                  | C-H, vinylidene (secondary alkyl group), CH <sub>2</sub> =C<  | Hydrocarbons, aliphatic  |
| 1635  | 6120                            | C-H Vinyl C-H, associated with (CH <sub>2</sub> =CH-)                                      | C-H, Vinyl (hexene), CH <sub>2</sub> =CH-   | Hydrocarbons, aliphatic  |
| 1637  | 6110                            | C-H from vinyl group as (CH <sub>2</sub> =CH-)   | C-H pendant vinyl group of the 1,2 unit for liquid carboxylated poly(acrylonitrile-co-butadiene) [or nitrile rubber (NBR)]          | C-H from vinyl associated group                                |
| 1654  | 6045                            | C-H Methyl C-H, nitro (CH <sub>3</sub> NO <sub>2</sub> )                                   | C-H methyl, CH <sub>3</sub> NO <sub>2</sub>   | Nitro (CH <sub>3</sub> ) as (CH <sub>3</sub> NO <sub>2</sub> ) |
| 1655  | 6025/6060 doublet               | C-H Methyl C-H, brominated (CH <sub>3</sub> Br)  | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> Br)                               |
| 1661  | 6020                            | C-H Methyl C-H, iodine (CH <sub>3</sub> I)   | C-H methyl, CH <sub>3</sub> I   | Halogenated (CH <sub>3</sub> I)                                |
| 1661  | 6000/6040 doublet               | C-H Methyl C-H, chlorinated CH <sub>3</sub>  | C-H methyl, CH <sub>3</sub> Cl  | Halogenated (CH <sub>3</sub> Cl)                               |
| 1664  | 6011                            | C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )                                     | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, Diols  |
| 1671  | 5985 (5988)                     | C-H Aromatic C-H (Aryl)  | CH <sub>v</sub> +CH <sub>v</sub> (12 + 1 ), Benzene band assignment   | C-H Aryl   |

(continued)

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |  |
|---|---------------------------------|---|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type  |
| 1678  | 5960                            | C-H Methyl C-H, carbonyl adjacent as (.C=OCH <sub>3</sub> )   | C-H methyl, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | Ketones  |
| 1680  | 5952                            | C-H Aromatic (ArCH)   | C-H (2ν), Aromatic C-H  | Hydrocarbons, aromatic   |
| 1680  | 5952                            | Wavelength – As defined in Classic Filter Instruments   | CH – Aromatic used as classic reference filter for filter instruments                   | Wavelength (No absorptions)  |
| 1682  | 5946                            | C-H Methyl C-H, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> )   | C-H methyl, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | Ketones  |
| 1685  | 5935                            | C-H Aromatic C-H  | C-H (2ν), ArC-H   | Hydrocarbons, aromatic   |
| 1688  | 5925                            | C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )  | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| 1689  | 5920 (5914)                     | C-H Aromatic C-H (Aryl)   | CH <sub>v</sub> +CH <sub>v</sub> (15 + 5), Benzene band assignment                      | C-H Aryl   |
| 1690  | 5915–5925                       | CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | CONH <sub>2</sub> specifically due to peptide β-sheet structures                        | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 1693  | 5905                            | C-H Methyl C-H branched   | C-H as RCH <sub>3</sub> CHR branched  | Aliphatic C-H  |
| 1693  | 5905                            | C-H Methyl C-H terminal   | C-H as R-CH <sub>3</sub> terminal   | Aliphatic C-H  |
| 1693  | 5908                            | C-H Methyl C-H, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> )   | C-H methyl, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | Ketones  |
| 1694  | 5903                            | C-H Methyl C-H, (.CH <sub>3</sub> ) (Asymmetric)  | C-H (2ν), Methyl C-H (Asymmetric)   | Hydrocarbons, Aliphatic  |
| 1694  | 5902                            | C-H Methyl C-H, iodine (CH <sub>3</sub> I)  | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> I)  |
| 1695  | 5900                            | C-H Methyl (.CH <sub>3</sub> )  | C-H (2ν), .CH <sub>3</sub>  | Hydrocarbons, Methyl   |
| 1695  | 5900 (gas phase)                | C-H Methyl C-H, brominated (CH <sub>3</sub> Br)   | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> Br)   |
| 1695  | 5898                            | C-H Methyl C-H, carbonyl adjacent as (.C=OCH <sub>3</sub> )   | C-H methyl, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | Ketones  |
| 1700  | 5882 (gas phase)                | C-H Methyl C-H, chlorinated (CH <sub>3</sub> Cl)  | C-H methyl, CH <sub>3</sub> Cl  | Halogenated (CH <sub>3</sub> Cl)   |
| 1701  | 5880                            | C-H Methyl C-H, Ether Associated as (R-O-CH <sub>3</sub> )  | C-H methyl, Ether Associated as R-O-CH <sub>3</sub>                                     | Ethers   |
| 1701  | 5880                            | C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )  | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| 1702  | 5874                            | C-H Methyl C-H, nitro (CH <sub>3</sub> NO <sub>2</sub> )  | C-H methyl, CH <sub>3</sub> NO <sub>2</sub>   | Nitro (CH <sub>3</sub> ) as (CH <sub>3</sub> NO <sub>2</sub> )                   |
| 1703  | 5872                            | C-H Methyl C-H branched   | C-H as RCH <sub>3</sub> CHR branched  | Aliphatic C-H  |
| 1704  | 5869                            | C-H Methyl C-H, (.CH <sub>3</sub> ) (Symmetric)   | C-H (2ν), Methyl C-H (Symmetric)  | Hydrocarbons, aliphatic  |
| 1705  | 5865                            | C-H Methyl (.CH <sub>3</sub> )  | C-H (2ν), .CH <sub>3</sub>  | Hydrocarbons, Methyl   |
| 1709  | 5853                            | C-H Methyl C-H terminal   | C-H as R-CH <sub>3</sub> terminal   | Aliphatic C-H  |
| 1711  | 5845                            | C-H Methyl C-H, iodine (CH <sub>3</sub> I)  | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> I)  |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |  |
|---|---------------------------------|---|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type  |
| 1725  | 5797                            | C-H Methylene (.CH <sub>2</sub> )   | C-H (2ν), .CH <sub>2</sub>  | Hydrocarbons, Methylene  |
| 1727  | 5787                            | C-H Methylene (.CH <sub>2</sub> ) (Asymmetric)  | C-H (2ν), Methylene C-H (Asymmetric)  | Hydrocarbons, aliphatic  |
| 1732  | 5773                            | C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )  | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| 1733  | 5770                            | C-H Methyl C-H, ether associated as (R-O-CH <sub>3</sub> )  | C-H methyl, Ether Associated as R-O-CH <sub>3</sub>   | Ethers   |
| 1735  | 5765                            | C-H Methyl C-H, amine associated as NH <sub>2</sub> CH <sub>3</sub>   | C-H methyl, Amine Associated as RN(CH <sub>3</sub> ) <sub>2</sub>   | Amines   |
| 1736  | 5760                            | C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )  | C-H methyl, aromatic (ArCH <sub>3</sub> )   | Aromatic (ArCH <sub>3</sub> )  |
| 1738  | 5755                            | CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the α-helix structure | CONH <sub>2</sub> specifically due to the α-helix peptide structure   | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 1740  | 5747                            | S-H Thiol (.S-H)  | S-H (2ν), .S-H  | Thiols   |
| 1744  | 5735                            | C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )  | C-H methyl, aromatic (ArCH <sub>3</sub> )   | Aromatic (ArCH <sub>3</sub> )  |
| 1748  | 5721                            | C-H (2ν) from silicone  | C-H (2ν) stretch from silicone (dimethyl siloxane)  | C-H from silicone (dimethyl siloxane)  |
| 1762  | 5675                            | C-H Methylene (.CH <sub>2</sub> ) (Symmetric)   | C-H (2ν), Methylene C-H (Symmetric)   | Hydrocarbons, aliphatic  |
| 1765  | 5666                            | C-H Methylene (.CH <sub>2</sub> )   | C-H (2ν), .CH <sub>2</sub>  | Hydrocarbons, methylene  |
| 1770  | 5650                            | C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )  | C-H methyl, aromatic (ArCH <sub>3</sub> )   | Aromatic (ArCH <sub>3</sub> )  |
| 1780  | 5618                            | C-H Methylene (.CH <sub>2</sub> )   | C-H (2ν), .CH <sub>2</sub>  | Cellulose  |
| 1790  | 5587                            | O-H from water  | O-H combination   | Water  |
| 1820  | 5495                            | O-H/C-H combination   | O-H stretching & C-O stretching (3ν <sub>s</sub> ) combination  | Cellulose  |
| 1860  | 5376                            | C-Cl Chlorinated organics (.C-Cl group)   | C-Cl (7ν), .C-Cl  | Chlorinated hydrocarbons   |
| 1892  | 5285                            | O-H hydrogen bonding between water and exposed polyvinyl alcohol OH   | O-H assigned as a one-to-one hydrogen-bonded to an isolated OH in the manner as OH::OH <sub>2</sub> from the effect of the hydration of the isolated alcohol OH – this pertains to the interactions of water with the OH groups in poly(ethylene-co-vinyl alcohol) (EVOH) | Water and polyvinyl alcohol OH   |
| 1900  | 5263                            | C=O Carbonyl (.C=OOH)   | C=O (3ν), .C=OOH  | Acids, carboxylic  |
| 1908  | 5241                            | P-OH Phosphate (.P-OH)  | O-H (2ν), .P-OH   | Phosphate  |
| 1920  | 5208                            | C=O Amide (.C=ONH)  | C=O (3ν), .C=ONH  | Amide  |
| (continued)   |                                 |   |   |  |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |   |
|---|---------------------------------|---|---|---|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type   |
| 1923  | 5200                            | O-H assigned to molecular water [O-H (.O-H & HOH)]                    | O-H assigned to molecular water (O-H stretching & HOH deformation combination)  | O-H molecular water   |
| 1928  | 5186                            | O-H (.O-H & HOH)  | O-H stretching & HOH deformation combination from water molecules in the 3-aminopropyltriethoxysilane-ethanol-water system  | O-H stretching & HOH deformation combination from 3-aminopropyltriethoxysilane-ethanol-water system |
| 1930  | 5181                            | O-H (.O-H & HOH)  | O-H stretching & HOH bending combination  | Polysaccharides   |
| 1933  | 5173                            | Si-O-H stretch + Si-O-Si combination from silicone                    | Si-O-H stretch + Si-O-Si deformation combination from silicone (dimethyl siloxane)  | Si-O-H stretch + Si-O-Si from silicone (dimethyl siloxane)  |
| 1938  | 5160                            | O-H Water at near 0 degrees C   | O-H (2v), .O-H — v <sub>2</sub> + v <sub>3</sub>  | Water   |
| 1940  | 5155                            | OH – Classic Filter Instrument  | Classic Filter Instrument   | Moisture (Classic)  |
| 1940  | 5155                            | O-H (H-O-H) Water   | O-H stretching & HOH bending combination  | Water   |
| 1942  | 5150                            | O-H hydrogen bonding between water and exposed polyvinyl alcohol OH   | O-H interaction of multiple hydrogen atoms from poly(ethylene-co-vinyl alcohol) (EVOH) bonded to surrounding associated OH groups (from water) without clustering | Water and polyvinyl alcohol OH  |
| 1950  | 5128                            | C=O Esters and Acids (.C=OOR)   | C=O (3v), .C=OOR  | Acids and esters  |
| 1960  | 5100                            | N-H combination band from primary amides (R-C=O – NH <sub>2</sub> )   | N-H [vN-H asymmetric & amide II deformation (N-H in-plane bending) combination] for primary amides  | N-H combination band from primary amides  |
| 1960  | 5102                            | O-H Polymeric (.O-H)  | O-H stretching & HOH bending combination  | Polysaccharides   |
| 1963.0  | 5095                            | N-H combination, primary aromatic amine ( <i>m</i> -NO <sub>2</sub> ) | N-H (vN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent   | Aromatic amine  |
| 1965  | 5090                            | O-H & CH combination from methanol                                    | v O-H & δC-H combination from CH <sub>3</sub> OH  | Methanol  |
| 1967.0  | 5084                            | N-H combination, primary aromatic amine ( <i>o</i> -NO <sub>2</sub> ) | N-H (vN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent  | Aromatic amine  |
| 1968.0  | 5082                            | N-H combination, primary aromatic amine ( <i>m</i> -Cl)               | N-H (vN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent  | Aromatic amine  |
| 1970.5  | 5075                            | N-H combination, primary aromatic amine ( <i>p</i> -Cl)               | N-H (vN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent  | Aromatic amine  |
| 1971.5  | 5072                            | N-H combination, primary aromatic amine (no other substituents)       | N-H (vN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> no other substituents   | Aromatic amine  |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |   |   |
|---|---------------------------------|--|---|---|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure   | Material Type                               |
| 1971.5  | 5072                            | N-H combination, primary aromatic amine (o-Cl)   | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping  | Aromatic amine                              |
| 1972  | 5071                            | N-H combination, from primary and secondary aromatic amine (mixtures of aniline and N-ethylaniline in CCl <sub>4</sub> ) | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent from primary and secondary aromatic amines | Primary and secondary aromatic amines       |
| 1975.5  | 5062                            | N-H combination, primary aromatic amine (p-CH <sub>3</sub> )   | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping                                  | Aromatic amine                              |
| 1977.5  | 5057                            | N-H combination, primary aromatic amine (o—OCH <sub>3</sub> )  | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent                             | Aromatic amine                              |
| 1980  | 5051                            | N-H Amide II (.CONH <sub>2</sub> )   | N-H stretching (asymmetric) & N-H in-plane bending combination  | Amides/proteins                             |
| 1980.5  | 5049                            | N-H combination, primary aromatic amine (p-NH <sub>2</sub> )   | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping                                  | Aromatic amine                              |
| 1990  | 5025                            | N-H Amide: NH <sub>2</sub> -C=ONH <sub>2</sub>   | N-H stretching & N-H bending combination  | Urea  |
| 1990  | 5025                            | N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | N-H [νN-H asymmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] for primary amides                         | N-H from urea                               |
| 2000  | 5000                            | N-H ammonia in water   | N-H (νN-H & δN-H combination) for NH <sub>3</sub> (ammonia) in water  | N-H (combination band) for ammonia in water |
| 2010  | 4975                            | N-H/C-N combination band from primary amides (R-C=O – NH <sub>2</sub> )  | N-H [νN-H symmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] for primary amides                          | N-H combination band from primary amides    |
| 2012  | 4970                            | N-H/C=O combination from Polyamide 11  | N-H/C=O [Bonded NH stretching & amide I (2νC=O stretching) combination] from polyamide 11   | Polyamide 11                                |
| 2016  | 4960                            | O-H stretching and bending combination from methanol   | ν O-H & δO-H combination from CH <sub>3</sub> OH  | Methanol O-H                                |
| 2024  | 4940                            | N-H/C=O combination from of native RNase A   | N-H/C=O [Bonded NH stretching & amide I (2νC=O stretching) combination] of native RNase A   | RNase A                                     |
| 2030  | 4926                            | C=O Amide: NH <sub>2</sub> -C=ONH <sub>2</sub>   | C=O (3ν), .C=ONH <sub>2</sub>   | Urea  |
| 2030  | 4925                            | N-H/C-N combination band from primary amides (R-C=O – NH <sub>2</sub> )  | N-H [νN-H asymmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] for primary amides                         | N-H combination band from primary amides    |
| (continued)   |                                 |  |   |   |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |  |  |
|---|---------------------------------|---|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure  | Material Type  |
| 2040  | 4902                            | N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )  | N-H [vN-H symmetric & amide II deformation (N-H in-plane bending) combination] for primary amides                            | N-H from urea  |
| 2050  | 4878                            | N-H combination band (RNase A) - C=O amide I band   | N-H native RNase A combination band at 4867cm <sup>-1</sup> shifting due to thermal unfolding (C=O amide I band).            | N-H from protein   |
| 2050  | 4878                            | N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> ) from native RNase A (thermal unfolding)   | N-H stretching & C=O stretching (Amide I) combination band observed in the thermal unfolding observed in native RNase A      | RNase A  |
| 2050  | 4878                            | N-H/C-N/N-H Amide II and Amide III combination (.CONH .) & .CONH <sub>2</sub> )   | N-H in-plane bend & C-N stretching & N-H in-plane bend combination   | Amides/proteins  |
| 2053  | 4870                            | N-H combination from polyamide 11   | Bonded NH stretching & amide II (N-H in-plane bending) from Polyamide 11   | Polyamide 11   |
| 2053  | 4867–4878                       | N-H band found at 4867 cm <sup>-1</sup> for native RNase A shifting to 4878 cm <sup>-1</sup> upon thermal unfolding.                                      | N-H from CONH <sub>2</sub> as thermal unfolding of RNase A protein in aqueous solution (Assigned to an N-H combination band) | Protein thermal unfolding  |
| 2055  | 4865                            | CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | CONH <sub>2</sub> specifically due to peptide β-sheet structures   | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2055  | 4867                            | N-H combination band (RNase A) - C=O amide I band   | N-H combination band found in the spectrum of native RNase A (C=O amide I band)  | N-H from protein   |
| 2055  | 4865                            | N-H from gamma-valerolactam   | N-H (vN-H & δN-H combination) for gamma-valerolactam   | Gamma-valerolactam   |
| 2055  | 4866                            | N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> )   | N-H stretching & C=O stretching (amide I) combination  | Amides/proteins  |
| 2055  | 4867                            | N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> ) from native RNase A   | N-H stretching & C=O stretching (amide I) combination band in the spectrum of native RNase A                                 | RNase A  |
| 2060  | 4855                            | HN...O=C band of Amide A  | CONH <sub>2</sub> combination of amide A and amide II  | Combination of amide A and amide II from proteins (polypeptides)                 |
| 2060  | 4854                            | N-H Amide as (.CONH .) & .CONH <sub>2</sub> )   | N-H (3δ) & N-H stretching combination  | Amides/proteins  |
| 2060  | 4850                            | N-H combination band from secondary amides in proteins  | N-H [vN-H & Amide II deformation (N-H in-plane bending) combination] for secondary amides in proteins                        | N-H from protein   |
| 2070  | 4831                            | N-H Amide: (N-H Deformation)  | N-H (δ)  | Urea   |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |  |   |
|---|---------------------------------|--|--|---|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure  | Material Type   |
| 2075  | 4820                            | N-H combination band from secondary amides in native RNase A   | N-H [ $\nu$ N-H & amide II deformation (N-H in-plane bending) combination] for secondary amides in native RNase A  | N-H from native RNase A   |
| 2080  | 4808                            | N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | N-H/C-N [ $\nu$ N-H asymmetric & amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea   | N-H/C-N from urea   |
| 2080  | 4808                            | O-H stretching and C-O bending combination from methanol   | $\nu$ O-H & $\delta$ O-H combination from CH <sub>3</sub> OH   | Methanol  |
| 2080  | 5550–4550 (broad)               | O-H broad band occurring in polyols, alcohols, water, ethylene vinyl alcohols and copolymers containing O-H groups                                 | O-H broad band, due to $\nu$ O-H & $\delta$ O-H combination  | Polyols, alcohols, water  |
| 2083  | 4800                            | O-H related combination from water change in phase and N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> ) from ovalbumin | O-H related combination from water change in phase with the increase in protein concentration at pH above 2.8 overlapping with a band representing the N-H/C-N [ $\nu$ <sub>s</sub> N-H asymmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] | O-H related combination from water change in phase and N-H/C-N from ovalbumin protein |
| 2090  | 4785                            | N-H from gamma-valerolactam  | N-H [NH stretching & amide II deformation (N-H in-plane bending) combination] for gamma-valerolactam   | Gamma-valerolactam  |
| 2090  | 4785                            | O-H Polymeric (.O-H)   | O-H combination  | Polymeric .OH   |
| 2096  | 4770                            | O-H deformation band, alcohols or water  | $3\delta$ O-H of mid infrared band occurring near 1420 cm <sup>-1</sup>  | Alcohols or water O-H   |
| 2100  | 4762                            | CHO – Classic Filter Instrument  | Classic Filter Instrument  | Carbohydrate (glucose)  |
| 2100  | 4762                            | C=O-O Polymeric (C=O and C-O stretching)   | C=O-O (4 $\nu$ )   | Polysaccharides (glucose)   |
| 2100  | 4762                            | O-H/C-O Polymeric (.O-H & .C-O)  | O-H bending & C-O stretching combination   | Polysaccharides (glucose)   |
| 2120  | 4715                            | N-H/C-N from gamma-valerolactam  | N-H/C-N [ $\nu$ N-H & amide III deformation (C-N stretching/N-H in-plane bending) combination] for gamma-valerolactam  | Gamma-valerolactam  |
| 2123  | 4710                            | O-H/C-O stretching combination from methanol   | $\nu$ O-H & $\nu$ C-O combination from CH <sub>3</sub> OH  | Methanol O-H  |
| 2127  | 4701                            | N-H/C=O combination from polyamide 11  | N-H/C=O [2 x Amide II (N-H in-plane bending) & amide I (2 $\nu$ C=O stretching) combination] from polyamide 11   | Polyamide 11  |
| (continued)   |                                 |  |  |   |



| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |  |  |
|---|---------------------------------|---|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure  | Material Type  |
| 2140  | 4673                            | C-H/C=O Lipid associated (.RC=CH & RC=O)  | C-H stretching & C=O stretching combination & C-H deformation combination  | Lipids   |
| 2145  | 4660                            | N-H/C-N/C=O from gamma-valerolactam   | N-H/C-N/C=O [2x amide I (2νC=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for gamma-valerolactam           | Gamma-valerolactam   |
| 2148  | 4655 (4675)                     | C-H Aromatic C-H (Aryl)   | CHv+CCv (15 + 9), Benzene band assignment  | C-H Aryl   |
| 2154  | 4642 (4644)                     | C-H Aromatic C-H (Aryl)   | CHv+CCv (12 + 16), Benzene band assignment   | C-H Aryl   |
| 2167  | 4615 (4625)                     | C-H Aromatic C-H (Aryl)   | CCv+CHv (16 + 5), Benzene band assignment  | C-H Aryl   |
| 2167  | 4615                            | CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the α-helix structure.  | CONH <sub>2</sub> specifically due to the α-helix peptide structure  | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2170  | 4608                            | C-H Alkenes (.HC=CH)  | C-H stretching & C-H deformation combination   | Alkenes  |
| 2174  | 4600                            | CONH <sub>2</sub> as combination of amide B and amide II modes (amide B/amide II) from ovalbumin  | CONH <sub>2</sub> as combination of amide B and amide II modes (amide B/amide II)  | Combination of amide B and amide II modes (amide B/amide II)                     |
| 2174  | 4600                            | CONH <sub>2</sub> specifically due to amide B and amide II modes (amide B/II) from ovalbumin protein side chains seen at shifting to lower wavenumber with considerable broadening at lowered pH (from pH 5.0 to 2.4) | CONH <sub>2</sub> specifically due to amide B and amide II modes (amide B/II).   | Proteins at low pH   |
| 2180  | 4587                            | N-H – Classic filter instrument   | N-H Classic filter instrument  | Protein  |
| 2180  | 4587                            | N-H Proteins: N-H (3ν <sub>B</sub> )  | N-H (3d)   | Proteins/amino acids   |
| 2180  | 4590                            | N-H/C-N/C=O combination band from secondary amides in proteins  | N-H/C-N/C=O [2x amide I (2νC=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for secondary amides in proteins | N-H/C-N/C=O from protein   |
| 2180  | 4687                            | N-H/C-N/C=O combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )  | N-H/C-N/C=O [2x amide I (2νC=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea                         | N-H/C-N/C=O from urea  |
| 2183  | 4586                            | N-H/C-N/N-H combination from polyamide 11   | N-H/C-N/N-H [Bonded NH stretching & amide III (C-N stretching/N-H in-plane bending) combination] from polyamide 11                                     | Polyamide 11   |
| 2188  | 4570 (4584)                     | C-H Aromatic C-H (Aryl)   | CCv+CHv (13 + 1), Benzene band assignment  | C-H Aryl   |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |  |  |
|---|---------------------------------|---|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure  | Material Type  |
| 2200  | 4545                            | CHO Carbohydrate (.CHO)   | C-H stretching & C=O combination   | Carbohydrates  |
| 2205  | 4535                            | N-H primary amine band of diamino- compound   | N-H (3v) band of primary amine as bisphenol A (I) resins cured with 4,4'-diaminodiphenyl sulfone (II) hardener               | Amine, primary   |
| 2206  | 4532 (4549)                     | C-H Aromatic C-H (Aryl)   | CCv+CHv (13 + 15), Benzene band assignment   | C-H Aryl   |
| 2207  | 4525–4540                       | CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | CONH <sub>2</sub> specifically due to peptide β-sheet structures   | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2210  | 4525                            | N-H ammonia in water  | N-H (3v) for NH <sub>3</sub> (ammonia) in water  | Ammonia in water   |
| 2212  | 4521                            | C=O/C-N/N-H combination from polyamide 11   | C=O/C-N/N-H [2 x amide I (2vC=O stretching) & amide III (C-N stretching/N-H in-plane bending) combination] from polyamide 11 | Polyamide 11   |
| 2220  | 4505                            | N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )  | N-H (vN-H asymmetric & NH <sub>2</sub> rocking) combination  | N-H from urea  |
| 2230  | 4484                            | CHO – Classic filter instrument   | Classic filter instrument  | Reference (Classic)  |
| 2270  | 4405                            | CHO – Classic filter instrument   | Classic Filter Instrument  | Lignin   |
| 2270  | 4405                            | CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | CONH <sub>2</sub> specifically due to peptide β-sheet structures   | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2270  | 4405                            | O-H/C-H Cellulose (.OH & .C-O)  | O-H stretching & C-O stretching combination  | Cellulose  |
| 2273  | 4400                            | O-H/C-O from glucose  | O-H/C-O Glucose absorption from O-H stretching & C-O stretching combination  | Glucose  |
| 2280  | 4386                            | C-H Starch (.C-H & CH <sub>2</sub> )  | C-H stretching & CH <sub>2</sub> deformation   | Polysaccharides  |
| 2290  | 4365–4370                       | CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the α-helix structure                                     | CONH <sub>2</sub> specifically due to the α-helix peptide structure  | Proteins as normalized 2nd-derivative spectra of proteins in aqueous solution    |
| 2294  | 4360 (4379)                     | C-H Aromatic C-H (Aryl)   | CHv+CHδ (12 + 3), Benzene band assignment  | C-H Aryl   |
| 2295  | 4357                            | C-H (3d) from silicone  | C-H (3δ) bend from silicone (dimethyl siloxane)  | C-H from silicone (dimethyl siloxane)  |
| 2300  | 4348                            | C-H (.C-H bending)  | C-H (3δ)   | Amides   |
| 2308  | 4333                            | C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>N</sub> R  | C-H (2vCH <sub>2</sub> Asymmetric stretching & δCH <sub>2</sub> ) combination  | Hydrocarbons, aliphatic  |
| 2310  | 4329                            | C-H (.C-H bending)  | C-H (3δ)   | Lipids   |

(continued)

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |   |   |  |
|---|---------------------------------|---|---|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type  |
| 2310  | 4329                            | CHO – Classic filter instrument   | Classic filter instrument   | Lipids/oils  |
| 2318  | 4314                            | C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub>                             | C-H (2νCH <sub>2</sub> Asymmetric stretching & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic  |
| 2322  | 4307                            | C-H (.C-H & CH <sub>2</sub> )   | C-H stretching & CH <sub>2</sub> deformation combination  | Polysaccharides (glucose)  |
| 2330  | 4292                            | C-H (.C-H & CH <sub>2</sub> )   | C-H stretching & CH <sub>2</sub> deformation combination  | Polysaccharides (glucose)  |
| 2335  | 4283                            | C-H (.C-H & CH <sub>2</sub> )   | C-H stretching & CH <sub>2</sub> deformation combination  | Polysaccharides (glucose)  |
| 2336  | 4281                            | CHO – Classic filter instrument   | Classic filter instrument   | Cellulose  |
| 2345  | 4265                            | C-H Methylene C-H, associated with ovalbumin protein side chains seen at pH 5.0   | C-H (2νCH <sub>2</sub> symmetric stretching & δCH <sub>2</sub> ) combination band from ovalbumin protein side chains seen at pH 5.0 | C-H from ovalbumin protein side chains   |
| 2347  | 4261                            | C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>N</sub> R  | C-H (2νCH <sub>2</sub> symmetric stretching & δCH <sub>2</sub> ) combination  | Hydrocarbons, aliphatic  |
| 2352  | 4252                            | C-H (.C-H bending)  | C-H (3δ)  | Polysaccharides  |
| 2352  | 4252 (4263)                     | C-H Aromatic C-H (Aryl)   | CH <sub>v</sub> +CH <sub>δ</sub> (12 + 17), Benzene band assignment   | C-H Aryl   |
| 2363  | 4232                            | C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub>                             | C-H (2νCH <sub>2</sub> symmetric stretching & δCH <sub>2</sub> ) combination  | Hydrocarbons, aliphatic  |
| 2380  | 4202                            | C-H/C-C (.C-H & .C-C)   | C-H stretching & C-C stretching combination   | Lipids   |
| 2387  | 4190 (4198)                     | C-H Aromatic C-H (Aryl)   | CC <sub>δ</sub> +CH <sub>v</sub> (17 + 5), Benzene band assignment  | C-H Aryl   |
| 2407  | 4155 (4175)                     | C-H Aromatic C-H (Aryl)   | CH <sub>v</sub> +CH <sub>δ</sub> (15 + 10), Benzene band assignment   | C-H Aryl   |
| 2440  | 4099                            | C-H Aromatic C-H (Aryl)   | CC <sub>δ</sub> +CH <sub>v</sub> (14 + 1 ), Benzene band assignment   | C-H Aryl   |
| 2444  | 4091                            | C-H Aromatic C-H (Aryl)   | CH <sub>v</sub> +CC <sub>v</sub> (12 + 2), Benzene band assignment  | C-H Aryl   |
| 2445  | 4090                            | CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the α-helix structure.                                    | CONH <sub>2</sub> specifically due to the α-helix peptide structure   | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2458  | 4068                            | C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>  | C-H (3δ CH <sub>3</sub> )   | Hydrocarbons, aliphatic  |
| 2463  | 4060                            | CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the β-sheet structure | CONH <sub>2</sub> specifically due to peptide β-sheet structures  | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| 2469  | 4050 (4060)                     | C-H Aromatic C-H (Aryl)   | CC <sub>δ</sub> +CH <sub>v</sub> (14 + 15), Benzene band assignment   | C-H Aryl   |

| In Ascending Wavelength and Descending Wavenumber Order (continued) |                                 |  |  |  |
|---|---------------------------------|--|--|--|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group   | Spectra Structure  | Material Type                            |
| 2470  | 4049                            | C-H (.CH <sub>2</sub> )  | C-H combination  | Lipids, aliphatic compounds              |
| 2470  | 4049                            | C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | C-H (3δ CH <sub>3</sub> )  | Hydrocarbons, aliphatic                  |
| 2470  | 4049                            | C-N-C Amide: (.C-N-C)  | C-N-C (2ν)   | Proteins                                 |
| 2477  | 4037                            | C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | C-H (3δ CH <sub>3</sub> )  | Hydrocarbons, aromatic                   |
| 2488  | 4019                            | C-H/C-C (.C-H & .C-C)  | C-H stretching & C-C stretching combination  | Cellulose                                |
| 2500  | 4000                            | C-H/C-C/C-O-C (.C-H & .C-C & .C-O-C)   | C-H stretching & C-C & C-O-C stretching combination  | Polysaccharides                          |
| 2513  | 3980                            | C-H Aromatic C-H (Aryl)  | CHv+CCδ (15 + 6), Benzene band assignment  | C-H Aryl                                 |
| 2525  | 3960                            | C-H Aromatic C-H (Aryl)  | CCω+CHv (19 + 15), Benzene band assignment   | C-H Aryl                                 |
| 2530  | 3953                            | C-N-C Amide: (.C-N-C)  | C-N-C (2ν) Asymmetric  | Amide                                    |
| 2540  | 3937                            | C-H Aromatic C-H (Aryl)  | CCω+CHv (11+ 12), Benzene band assignment  | C-H Aryl                                 |
| 2679  | 3733                            | C-H Aromatic C-H (Aryl)  | CHω+CHv ( 4 + 1 ), Benzene band assignment   | C-H Aryl                                 |
| 2687  | 3722                            | C-H Aromatic C-H (Aryl)  | CCω+CHv (7 + 5), Benzene band assignment   | C-H Aryl                                 |
| 2708  | 3693                            | C-H Aromatic C-H (Aryl)  | CCω+CHv ( 8 + 5), Benzene band assignment  | C-H Aryl                                 |
| 2740  | 3650                            | O-H from primary alcohols as (-CH <sub>2</sub> -OH)  | O-H (ν) (-CH <sub>2</sub> -OH), Primary alcohols   | Primary alcohols                         |
| 2747  | 3640                            | C-H Aromatic C-H (Aryl)  | CHv+CCδ (12+18), Benzene band assignment   | C-H Aryl                                 |
| 2762  | 3620                            | O-H from secondary alcohols as (-CH-OH)  | O-H (ν) (-CH-OH), Secondary alcohols   | Secondary alcohols                       |
| 2768  | 3613                            | C-H Aromatic C-H (Aryl)  | CCω+CHv (18 + 5), Benzene band assignment  | C-H Aryl                                 |
| 2770  | 3610                            | O-H from tertiary alcohols as (-C-OH)  | O-H (ν) (-C-OH), Tertiary alcohols   | Tertiary alcohols                        |
| 3030  | 3300                            | CONH <sub>2</sub> (HN...O=C band) of Amide A   | CONH <sub>2</sub> as amide A for the polypeptides  | Amide A from proteins (polypeptides)     |
| 3049  | 3280                            | O-H stretching vibration (ν) of water molecules in bound-water hydrogen bonding in turquoise minerals                      | O-H ν (as intense and very broad band assigned to bound-water hydrogen bonding in turquoise minerals from Arizona and Senegal with a formula of Cu(Al <sub>6-x</sub> Fe <sub>x</sub> )(PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>8</sub> ·4H <sub>2</sub> O | Bound-water hydrogen bonding in minerals |
| (continued)   |                                 |  |  |  |

| In Ascending Wavelength and Descending Wavenumber Order (continued)   |                                 |   |   |                                |
|---|---------------------------------|---|---|--------------------------------|
| Nanometers (nm)   | Wavenumbers (cm <sup>-1</sup> ) | Functional Group  | Spectra Structure   | Material Type                  |
| 3067  | 3260                            | O-H stretching vibration ( $\nu$ ) of water molecules in protein-water hydrogen bonding | O-H $\nu$ (as intense and very broad band assigned to protein-water hydrogen bonding) | Protein-water hydrogen bonding |
| 3521  | 2840                            | O-H stretching vibrations of water molecules in water-water hydrogen bonding            | O-H as intense and very broadband assigned to water-water hydrogen bonding            | Water-water hydrogen bonding   |
| <i>Notes:</i> 1 $\nu$ , fundamental stretching vibrational absorption band; 2 $\nu$ , first overtone of fundamental stretching band; 3 $\nu$ , second overtone of fundamental stretching band; 4 $\nu$ , third overtone of fundamental stretching band; 5 $\nu$ , fourth overtone of fundamental stretching band; 6 $\nu$ , fifth overtone of fundamental stretching band; 1 $\delta$ , fundamental bending vibrational absorption band; 2 $\delta$ , first overtone of fundamental bending band; 3 $\delta$ , second overtone of fundamental bending band; 4 $\delta$ , third overtone of fundamental bending band; $\omega$ , deformation (rocking or wagging). |                                 |   |   |                                |

| In Ascending Alphabetical Functional Group Order           |                 |                                 |  |                                       |
|--|-----------------|---------------------------------|--|---------------------------------------|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type                         |
| C-Cl Chlorinated organics (.C-Cl group)                    | 1860            | 5376                            | C-Cl (7v), .C-Cl   | Chlorinated hydrocarbons              |
| C-H (.C-H & CH <sub>2</sub> )                              | 2322            | 4307                            | C-H stretching & CH <sub>2</sub> deformation combination | Polysaccharides (glucose)             |
| C-H (.C-H & CH <sub>2</sub> )                              | 2330            | 4292                            | C-H stretching & CH <sub>2</sub> deformation combination | Polysaccharides (glucose)             |
| C-H (.C-H & CH <sub>2</sub> )                              | 2335            | 4283                            | C-H stretching & CH <sub>2</sub> deformation combination | Polysaccharides (glucose)             |
| C-H (.C-H bending)   | 2300            | 4348                            | C-H (3δ)   | Amides                                |
| C-H (.C-H bending)   | 2310            | 4329                            | C-H (3δ)   | Lipids                                |
| C-H (.C-H bending)   | 2352            | 4252                            | C-H (3δ)   | Polysaccharides (glucose)             |
| C-H (.CH <sub>2</sub> )                                    | 2470            | 4049                            | C-H combination  | Lipids, aliphatic compounds           |
| C-H (2v) from silicone                                     | 1748            | 5721                            | C-H (2v) stretch from silicone (dimethyl siloxane)       | C-H from silicone (dimethyl siloxane) |
| C-H (3d) from silicone                                     | 2295            | 4357                            | C-H (3δ) bend from silicone (dimethyl siloxane)          | C-H from silicone (dimethyl siloxane) |
| C-H (Aromatic C-H)   | 1143            | 8749                            | C-H (3v), Ar.C-H   | Hydrocarbons, aromatic                |
| C-H Acrylate C-H as (CH <sub>2</sub> =CHCOO <sup>-</sup> ) | 1621            | 6169                            | C- H, combination of two stretching modes                | Acrylate                              |
| C-H Alkene (.HC=CH)  | 1170            | 8547                            | C-H (3v), .HC=CH   | Alkenes, polyenes                     |
| C-H Alkene, .=CH <sub>2</sub>                              | 1620            | 6173                            | C-H (2v), .=CH <sub>2</sub>                              | Alkenes                               |
| C-H Alkenes (.HC=CH)                                       | 2170            | 4608                            | C-H stretching & C-H deformation combination             | Alkenes                               |
| C-H Aromatic (ArCH)  | 714             | 13986                           | C-H (5v), Aromatic; C-H                                  | Hydrocarbons, aromatic                |
| C-H Aromatic (ArCH)  | 876             | 11655                           | C-H (4v), Aromatic; C-H                                  | Hydrocarbons, aromatic                |
| C-H Aromatic (ArCH)  | 1142            | 8754                            | C-H (3v), Aromatic; C-H                                  | Hydrocarbons, aromatic                |
| C-H Aromatic (ArCH)  | 1680            | 5952                            | C-H (2v), Aromatic; C-H                                  | Hydrocarbons, aromatic                |
| C-H Aromatic (ArC-H)                                       | 1446            | 6916                            | C-H combination, ArC-H                                   | Hydrocarbons, aromatic                |
| C-H Aromatic C-H   | 1417            | 7057                            | C-H combination, Ar.C-H                                  | Hydrocarbons, aromatic                |
| C-H Aromatic C-H   | 1685            | 5935                            | C-H (2v), ArC-H  | Hydrocarbons, aromatic                |
| C-H Aromatic C-H (Aryl)                                    | 1671            | 5985 (5988)                     | CHv+CHv (12 + 1 ), Benzene band assignment               | C-H Aryl                              |
| C-H Aromatic C-H (Aryl)                                    | 1689            | 5920 (5914)                     | CHv+CHv (15 + 5), Benzene band assignment                | C-H Aryl                              |
| C-H Aromatic C-H (Aryl)                                    | 2148            | 4655 (4675)                     | CHv+CCv (15 + 9), Benzene band assignment                | C-H Aryl                              |
| C-H Aromatic C-H (Aryl)                                    | 2154            | 4642 (4644)                     | CHv+CCv (12 + 16), Benzene band assignment               | C-H Aryl                              |
| C-H Aromatic C-H (Aryl)                                    | 2167            | 4615 (4625)                     | CCv+CHv (16 + 5), Benzene band assignment                | C-H Aryl                              |

(continued)

| In Ascending Alphabetical Functional Group Order (continued) |                 |                                 |  |                                 |
|--|-----------------|---------------------------------|--|---------------------------------|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type                   |
| C-H Aromatic C-H (Aryl)                                      | 2188            | 4570 (4584)                     | CCv+CHv (13 + 1), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2206            | 4532 (4549)                     | CCv+CHv (13 + 15), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2294            | 4360 (4379)                     | CHv+CHδ (12 + 3), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2352            | 4252 (4263)                     | CHv+CHδ (12 + 17), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2387            | 4190 (4198)                     | CCδ+CHv (17 + 5), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2407            | 4155 (4175)                     | CHv+CHδ (15 + 10), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2440            | 4099                            | CCδ+CHv (14 + 1), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2444            | 4091                            | CHv+CCv (12 + 2), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2469            | 4050 (4060)                     | CCδ+CHv (14 + 15), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2513            | 3980 (3986)                     | CHv+CCδ (15 + 6), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2525            | 3960 (3958)                     | CCω+CHv (19 + 15), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2540            | 3937 (3935)                     | CCω+CHv (11+ 12), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2679            | 3733                            | CHω+CHv ( 4 + 1 ), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2687            | 3722 (3735)                     | CCω+CHv (7 + 5), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2708            | 3693 (3697)                     | CCω+CHv ( 8 + 5), Benzene band assignment  | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2747            | 3640 (3643)                     | CHv+CCδ (12 + 18), Benzene band assignment   | C-H Aryl                        |
| C-H Aromatic C-H (Aryl)                                      | 2768            | 3613 (3613)                     | CCω+CHv (18 + 5), Benzene band assignment  | C-H Aryl                        |
| C-H from vinyl group as (CH <sub>2</sub> =CH- )              | 1637            | 6110                            | C-H pendant vinyl group of the 1,2 unit for liquid carboxylated poly(acrylonitrile-co-butadiene) [or nitrile rubber (NBR)] | C-H from vinyl associated group |
| C-H Methyl (.CH <sub>3</sub> )                               | 908             | 11052–10953                     | C-H (4v), .CH <sub>3</sub>   | Hydrocarbons, methyl            |
| C-H Methyl (.CH <sub>3</sub> )                               | 1195            | 8368                            | C-H (3v), .C-H <sub>3</sub>  | Hydrocarbons, aliphatic         |
| C-H Methyl (.CH <sub>3</sub> )                               | 1360            | 7353                            | C-H combination, .C-H <sub>3</sub>   | Hydrocarbons, aliphatic         |
| C-H Methyl (.CH <sub>3</sub> )                               | 1695            | 5900                            | C-H (2v), .CH <sub>3</sub>   | Hydrocarbons, methyl            |
| C-H Methyl (.CH <sub>3</sub> )                               | 1705            | 5865                            | C-H (2v), .CH <sub>3</sub>   | Hydrocarbons, methyl            |
| C-H Methyl C-H branched                                      | 1693            | 5905                            | C-H as RCH <sub>3</sub> CHR branched   | Aliphatic C-H                   |
| C-H Methyl C-H branched                                      | 1703            | 5872                            | C-H as RCH <sub>3</sub> CHR branched   | Aliphatic C-H                   |

| In Ascending Alphabetical Functional Group Order (continued)   |                 |                                 |   |                                  |
|--|-----------------|---------------------------------|---|----------------------------------|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type                    |
| C-H Methyl C-H terminal  | 1693            | 5905                            | C-H as R-CH <sub>3</sub> terminal                                     | Aliphatic C-H                    |
| C-H Methyl C-H terminal  | 1709            | 5853                            | C-H as R-CH <sub>3</sub> terminal                                     | Aliphatic C-H                    |
| C-H Methyl C-H, (.CH <sub>3</sub> )  | 747             | 13387                           | C-H (5v), Methyl; C-H   | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, (.CH <sub>3</sub> )  | 915             | 10929                           | C-H (4v), Methyl; C-H   | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, (.CH <sub>3</sub> )  | 1194            | 8375                            | C-H (3v), Methyl; C-H   | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, (.CH <sub>3</sub> ) (Asymmetric)   | 1694            | 5903                            | C-H (2v), Methyl; C-H (Asymmetric)                                    | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, (.CH <sub>3</sub> ) (Symmetric)  | 1704            | 5869                            | C-H (2v), Methyl; C-H (Symmetric)                                     | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, amine associated as NH <sub>2</sub> CH <sub>3</sub>  | 1735            | 5765                            | C-H methyl, amine Associated as RN(CH <sub>3</sub> ) <sub>2</sub>     | Amines                           |
| C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )   | 1736            | 5760                            | C-H methyl, aromatic (ArCH <sub>3</sub> )                             | Aromatic (ArCH <sub>3</sub> )    |
| C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )   | 1744            | 5735                            | C-H methyl, aromatic (ArCH <sub>3</sub> )                             | Aromatic (ArCH <sub>3</sub> )    |
| C-H Methyl C-H, aromatic associated (ArCH <sub>3</sub> )   | 1770            | 5650                            | C-H methyl, aromatic (ArCH <sub>3</sub> )                             | Aromatic (ArCH <sub>3</sub> )    |
| C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | 803             | 12453                           | C-H (4vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aromatic           |
| C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | 1021            | 9796                            | C-H (3vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aromatic           |
| C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | 1370            | 7300                            | C-H (2vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aromatic           |
| C-H Methyl C-H, associated with aromatic (ArCH <sub>3</sub> )  | 2477            | 4037                            | C-H (3δ CH <sub>3</sub> )   | Hydrocarbons, aromatic           |
| C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 813             | 12300                           | C-H (4vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 1021            | 9794                            | C-H (3vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 1396            | 7163                            | C-H (2vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 2470            | 4049                            | C-H (3δ CH <sub>3</sub> )   | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>           | 796             | 12563                           | C-H (4vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>           | 1021            | 9795                            | C-H (3vCH <sub>3</sub> & δCH <sub>3</sub> ) combination               | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>           | 1390            | 7194                            | C-H (2v <sub>s</sub> CH <sub>3</sub> & δCH <sub>3</sub> ) combination | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, associated with linear aliphatic CH <sub>3</sub> (CH <sub>2</sub> ) <sub>N</sub> CH <sub>3</sub>           | 2458            | 4068                            | C-H (3δ CH <sub>3</sub> )   | Hydrocarbons, aliphatic          |
| C-H Methyl C-H, brominated (CH <sub>3</sub> Br)  | 1650/1660       | 6060/6025 doublet               | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> Br) |
| (continued)  |                 |                                 |   |                                  |



| In Ascending Alphabetical Functional Group Order (continued)                                |                 |                                 |   |  |
|---|-----------------|---------------------------------|---|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type  |
| C-H Methyl C-H, brominated (CH <sub>3</sub> Br)   | 1695            | 5900 (gas phase)                | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> Br)                               |
| C-H Methyl C-H, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | 1678            | 5960                            | C-H methyl, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | Ketones  |
| C-H Methyl C-H, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | 1695            | 5898                            | C-H methyl, carbonyl adjacent as (.C=OCH <sub>3</sub> )                                 | Ketones  |
| C-H Methyl C-H, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | 1682            | 5946                            | C-H methyl, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | Ketones  |
| C-H Methyl C-H, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | 1693            | 5908                            | C-H methyl, carbonyl associated as one C removed (.C=OCH <sub>2</sub> CH <sub>3</sub> ) | Ketones  |
| C-H Methyl C-H, chlorinated (CH <sub>3</sub> Cl)  | 1700            | 5882 (gas phase)                | C-H methyl, CH <sub>3</sub> Cl  | Halogenated (CH <sub>3</sub> Cl)                               |
| C-H Methyl C-H, chlorinated CH <sub>3</sub>   | 1656/1667       | 6040/ 6000 doublet              | C-H methyl, CH <sub>3</sub> Cl  | Halogenated (CH <sub>3</sub> Cl)                               |
| C-H Methyl C-H, ether associated as (R-O-CH <sub>3</sub> )                                  | 1701            | 5880                            | C-H methyl, ether associated as R-O-CH <sub>3</sub>                                     | Ethers   |
| C-H Methyl C-H, ether associated as (R-O-CH <sub>3</sub> )                                  | 1733            | 5770                            | C-H methyl, ether associated as R-O-CH <sub>3</sub>                                     | Ethers   |
| C-H Methyl C-H, iodine (CH <sub>3</sub> I)  | 1661            | 6020                            | C-H methyl, CH <sub>3</sub> I   | Halogenated (CH <sub>3</sub> I)                                |
| C-H Methyl C-H, iodine (CH <sub>3</sub> I)  | 1694            | 5902                            | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> I)                                |
| C-H Methyl C-H, iodine (CH <sub>3</sub> I)  | 1711            | 5845                            | C-H methyl, CH <sub>3</sub> Br  | Halogenated (CH <sub>3</sub> I)                                |
| C-H Methyl C-H, nitro (CH <sub>3</sub> NO <sub>2</sub> )                                    | 1654            | 6045                            | C-H methyl, CH <sub>3</sub> NO <sub>2</sub>   | Nitro (CH <sub>3</sub> ) as (CH <sub>3</sub> NO <sub>2</sub> ) |
| C-H Methyl C-H, nitro (CH <sub>3</sub> NO <sub>2</sub> )                                    | 1702            | 5874                            | C-H methyl, CH <sub>3</sub> NO <sub>2</sub>   | Nitro (CH <sub>3</sub> ) as (CH <sub>3</sub> NO <sub>2</sub> ) |
| C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )                                      | 1664            | 6011                            | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )                                      | 1688            | 5925                            | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )                                      | 1701            | 5880                            | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| C-H Methyl C-H, OH associated as (ROHCH <sub>3</sub> )                                      | 1732            | 5773                            | C-H methyl, OH associated as ROHCH <sub>3</sub>   | Alcohols, diols  |
| C-H Methylene (.CH <sub>2</sub> )   | 762             | 13123                           | C-H (5v), Methylene C-H   | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 930             | 10811–10695                     | C-H (4v), .CH <sub>2</sub>  | Hydrocarbons, methylene  |
| C-H Methylene (.CH <sub>2</sub> )   | 930             | 10753                           | C-H (4v), Methylene C-H   | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1211            | 8258                            | C-H (3v), Methylene C-H   | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1215            | 8230                            | C-H (3v), .C-H <sub>2</sub>   | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1395            | 7168                            | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1415            | 7067                            | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1440            | 6944                            | C-H combination, .C-H <sub>2</sub>  | Hydrocarbons, aliphatic  |
| C-H Methylene (.CH <sub>2</sub> )   | 1725            | 5797                            | C-H (2v), .CH <sub>2</sub>  | Hydrocarbons, methylene  |

| In Ascending Alphabetical Functional Group Order (continued)  |                 |                                 |   |  |
|---|-----------------|---------------------------------|---|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type                          |
| C-H Methylene (.CH <sub>2</sub> )   | 1765            | 5666                            | C-H (2ν), .CH <sub>2</sub>  | Hydrocarbons, methylene                |
| C-H Methylene (.CH <sub>2</sub> )   | 1780            | 5618                            | C-H (2ν), .CH <sub>2</sub>  | Cellulose                              |
| C-H Methylene (.CH <sub>2</sub> ) (Asymmetric)  | 1727            | 5787                            | C-H (2ν), Methylene; C-H (Asymmetric)   | Hydrocarbons, aliphatic                |
| C-H Methylene (.CH <sub>2</sub> ) (Symmetric)   | 1762            | 5675                            | C-H (2ν), Methylene; C-H (Symmetric)  | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 836             | 11962                           | C-H (4νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 1042            | 9600                            | C-H (3νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 1411            | 7085                            | C-H (2νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 2318            | 4314                            | C-H (2νCH <sub>2</sub> Asymmetric stretching & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with branched aliphatic RC(CH <sub>3</sub> ) <sub>3</sub> or RCH(CH <sub>3</sub> ) <sub>2</sub> | 2363            | 4232                            | C-H (2νCH <sub>2</sub> Symmetric stretching & δCH <sub>2</sub> ) combination  | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>n</sub> R  | 830             | 12048                           | C-H (4νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>n</sub> R  | 1041            | 9606                            | C-H (3νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>n</sub> R  | 1410            | 7092                            | C-H (2νCH <sub>2</sub> & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>n</sub> R  | 2308            | 4333                            | C-H (2νCH <sub>2</sub> Asymmetric stretching & δCH <sub>2</sub> ) combination   | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with linear aliphatic R(CH <sub>2</sub> ) <sub>n</sub> R  | 2347            | 4261                            | C-H (2νCH <sub>2</sub> Symmetric stretching & δCH <sub>2</sub> ) combination  | Hydrocarbons, aliphatic                |
| C-H Methylene C-H, associated with ovalbumin protein side chains seen at pH 5.0   | 2345            | 4265                            | C-H (2νCH <sub>2</sub> symmetric stretching & δCH <sub>2</sub> ) combination band from ovalbumin protein side chains seen at pH 5.0 | C-H from ovalbumin protein side chains |
| C-H Alkyne C-H as (R-C-C≡C-H)   | 1530            | 6536                            | C-H, Alkyne (1-hexyne) as (R-C-C≡C-H)   | Acetylene or Alkyne C-H                |
| C-H Secondary or Tertiary Carbon (.CH)  | 1225            | 8163                            | C-H (3ν), .C-H  | Hydrocarbons, aliphatic                |
| C-H Starch (.C-H & CH <sub>2</sub> )  | 2280            | 4386                            | C-H stretching & CH <sub>2</sub> deformation  | Polysaccharides (glucose)              |
| C-H Vinyl and vinylidene C-H as (CH <sub>2</sub> =C(CH <sub>3</sub> )-CH=CH <sub>2</sub> )                                    | 1630            | 6135                            | C-H, Vinyl and vinylidene (2-methyl-1,3-butadiene), isoprene as (CH <sub>2</sub> =C(CH <sub>3</sub> )-CH=CH <sub>2</sub> )          | Vinyl and vinylidene C-H as isoprene   |

(continued)

| In Ascending Alphabetical Functional Group Order (continued)               |                 |                                 |  |   |
|--|-----------------|---------------------------------|--|---|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type   |
| C-H Vinyl C-H attached to >C=O group, such as (CH <sub>2</sub> =CH-C=O - ) | 1613            | 6200                            | C-H, Vinyl on O (1-ethenyloxybutane) as (CH <sub>2</sub> =CH-C=O - )   | Vinyl as 1-ethenyl oxybutane (1-ethenyl- methyl-ethyl-ketone) |
| C-H Vinyl C-H attached to N group, such as (CH <sub>2</sub> =CH-N-C=O - C) | 1621            | 6170                            | C-H, Vinyl on N (1-ethenyl 2-pyrrolidinone) as (CH <sub>2</sub> =CH-N-C=O - C)   | Vinyl on pyrrolidinone  |
| C-H Vinyl C-H, associated with (CH <sub>2</sub> =CH-)                      | 1635            | 6120                            | C-H, Vinyl (hexene), CH <sub>2</sub> =CH-  | Hydrocarbons, aliphatic                                       |
| C-H Vinylidene C-H, associated with (CH <sub>2</sub> =C<)                  | 1631            | 6130                            | C-H, Vinylidene (secondary alkyl group), CH <sub>2</sub> =C<   | Hydrocarbons, aliphatic                                       |
| C-H/C=O Lipid associated (.RC=CH & RC=O)                                   | 2140            | 4673                            | C-H stretching & C=O stretching combination & C-H deformation combination  | Lipids  |
| C-H/C-C (.C-H & .C-C)  | 2380            | 4202                            | C-H stretching & C-C stretching combination  | Lipids  |
| C-H/C-C (.C-H & .C-C)  | 2488            | 4019                            | C-H stretching & C-C Stretching Combination  | Cellulose   |
| C-H/C-C/C-O-C (.C-H & .C-C & .C-O-C)                                       | 2500            | 4000                            | C-H stretching & C-C & C-O-C stretching combination  | Polysaccharides   |
| CHO – Classic filter instrument  | 2100            | 4762                            | Classic filter instrument  | Carbohydrate  |
| CHO – Classic filter instrument  | 2230            | 4484                            | Classic filter instrument  | Reference (Classic)   |
| CHO – Classic filter instrument  | 2270            | 4405                            | Classic filter instrument  | Lignin  |
| CHO – Classic filter instrument  | 2310            | 4329                            | Classic filter instrument  | Lipids/oils   |
| CHO – Classic filter instrument  | 2336            | 4281                            | Classic filter instrument  | Cellulose   |
| CHO Carbohydrate (.CHO)  | 2200            | 4545                            | C-H stretching & C=O combination   | Carbohydrates   |
| C-N-C Amide: (.C-N-C)  | 2470            | 4049                            | C-N-C (2v)   | Proteins  |
| C-N-C Amide: (.C-N-C)  | 2530            | 3953                            | C-N-C (2v) Asymmetric  | Amide   |
| C=O (Carbonyl >C=O)  | 1160            | 8621                            | C=O (5v)   | Hydrocarbons, aliphatic                                       |
| C=O (Carbonyl >C=O)  | 1450            | 6897                            | C=O (4v)   | Ketones & aldehydes   |
| C=O Amide (.C=ONH)   | 1920            | 5208                            | C=O (3v), .C=ONH   | Amide   |
| C=O Amide: NH <sub>2</sub> -C=ONH <sub>2</sub>                             | 2030            | 4926                            | C=O (3v), .C=ONH <sub>2</sub>  | Urea  |
| C=O Carbonyl (.C=OOH)  | 1900            | 5263                            | C=O (3v), .C=OOH   | Acids, Carboxylic   |
| C=O Esters and acids (.C=OOR)  | 1950            | 5128                            | C=O (3v), .C=OOR   | Acids and esters  |
| C=O/C-N/N-H combination from polyamide 11                                  | 2212            | 4521                            | C=O/C-N/N-H [2 x amide I (2vC=O stretching) & amide III (C-N stretching/N-H in-plane bending) combination] from polyamide 11 | Polyamide 11  |
| C=O/N-H combination from polyamide 11                                      | 1598            | 6256                            | C=O/N-H [Amide I (2v <sub>s</sub> C=O stretching) & 3 x amide II (N-H in-plane bending) combination] from polyamide 11       | Polyamide 11  |
| C=O-O Polymeric (C=O and C-O stretching)                                   | 2100            | 4762                            | C=O-O (4v)   | Polysaccharides (glucose)                                     |

| In Ascending Alphabetical Functional Group Order (continued)  |                 |                                 |   |  |
|---|-----------------|---------------------------------|---|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type  |
| CONH <sub>2</sub> (HN...O=C band) of Amide A  | 3030            | 3300                            | CONH <sub>2</sub> as amide A for the polypeptides                                 | Amide A from proteins (polypeptides)   |
| CONH <sub>2</sub> as combination of amide B and amide II modes (amide B/amide II) from ovalbumin  | 2174            | 4600                            | CONH <sub>2</sub> as combination of amide B and amide II modes (amide B/amide II) | Combination of amide B and amide II modes (amide B/amide II)                     |
| CONH <sub>2</sub> specifically due to amide B and amide II modes (amide B/II) from ovalbumin protein side chains seen at shifting to lower wavenumber with considerable broadening at lowered pH (from pH 5.0 to 2.4) | 2174            | 4600                            | CONH <sub>2</sub> specifically due to amide B and amide II modes (amide B/II)     | Proteins at low pH   |
| CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the $\alpha$ -helix structure   | 1738            | 5755                            | CONH <sub>2</sub> specifically due to the $\alpha$ -helix peptide structure       | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the $\alpha$ -helix structure   | 2167            | 4615                            | CONH <sub>2</sub> specifically due to the $\alpha$ -helix peptide structure       | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the $\alpha$ -helix structure   | 2290            | 4365–4370                       | CONH <sub>2</sub> specifically due to the $\alpha$ -helix peptide structure       | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to C=O hydrogen bonded to the N-H of the peptide link termed the $\alpha$ -helix structure   | 2445            | 4090                            | CONH <sub>2</sub> specifically due to the $\alpha$ -helix peptide structure       | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the $\beta$ -sheet structure  | 1690            | 5915–5925                       | CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures           | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the $\beta$ -sheet structure  | 2055            | 4865                            | CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures           | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the $\beta$ -sheet structure  | 2208            | 4525–4540                       | CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures           | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the $\beta$ -sheet structure  | 2270            | 4405                            | CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures           | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| CONH <sub>2</sub> specifically due to peptide N-H and C=O groups at right angles to the line of the peptide backbone referred to as the $\beta$ -sheet structure  | 2463            | 4060                            | CONH <sub>2</sub> specifically due to peptide $\beta$ -sheet structures           | Proteins as normalized second-derivative spectra of proteins in aqueous solution |
| (continued)   |                 |                                 |   |  |

| In Ascending Alphabetical Functional Group Order (continued)  |                 |                                 |  |  |
|---|-----------------|---------------------------------|--|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type  |
| HN...O=C band of Amide A  | 2060            | 4855                            | CONH <sub>2</sub> combination of amide A and amide II  | Combination of amide A and amide II from proteins (polypeptides) |
| N-H – Classic filter instrument   | 2180            | 4587                            | N-H Classic filter instrument  | Protein  |
| N-H from primary and secondary aromatic amine (mixtures of aniline and N-ethylaniline in CCl <sub>4</sub> ) | 1493            | 6698                            | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent | Aromatic amines  |
| N-H primary aromatic amine ( <i>m</i> -Cl)  | 1018.5          | 9818                            | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent               | Aromatic amine   |
| N-H primary aromatic amine ( <i>m</i> -Cl)  | 1445.0          | 6920                            | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent               | Aromatic amine   |
| N-H primary aromatic amine ( <i>m</i> -Cl)  | 1489.5          | 6713                            | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent                | Aromatic amine   |
| N-H primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )  | 1015.0          | 9852                            | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent  | Aromatic amine   |
| N-H primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )  | 1441.0          | 6940                            | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent  | Aromatic amine   |
| N-H primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )  | 1487.0          | 6725                            | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent   | Aromatic amine   |
| N-H primary aromatic amine (no other substituents)  | 1021.0          | 9794                            | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                | Aromatic amine   |
| N-H primary aromatic amine (no other substituents)  | 1448.5          | 6904                            | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                | Aromatic amine   |
| N-H primary aromatic amine (no other substituents)  | 1493.0          | 6698                            | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> no other substituents                 | Aromatic amine   |
| N-H primary aromatic amine ( <i>o</i> -Cl)  | 1017.5          | 9828                            | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping                 | Aromatic amine   |
| N-H primary aromatic amine ( <i>o</i> -Cl)  | 1443.0          | 6930                            | N-H (2ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping                 | Aromatic amine   |
| N-H primary aromatic amine ( <i>o</i> -Cl)  | 1491.5          | 6705                            | N-H (2ν) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping                  | Aromatic amine   |
| N-H primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )  | 1003.0          | 9970                            | N-H (3ν) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent | Aromatic amine   |

| In Ascending Alphabetical Functional Group Order (continued) |                 |                                 |   |                |
|--|-----------------|---------------------------------|---|----------------|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type  |
| N-H primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )     | 1432.0          | 6982                            | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent  | Aromatic amine |
| N-H primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )     | 1472            | 6791                            | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent   | Aromatic amine |
| N-H primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> )    | 1018.5          | 9818                            | N-H (3v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent | Aromatic amine |
| N-H primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> )    | 1446.0          | 6916                            | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent | Aromatic amine |
| N-H primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> )    | 1492.5          | 6700                            | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent  | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )     | 1023.0          | 9775                            | N-H (3v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping      | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )     | 1452.5          | 6885                            | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping      | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )     | 1496.5          | 6683                            | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping       | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -Cl)                   | 1019.0          | 9813                            | N-H (3v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -Cl)                   | 1448.0          | 6906                            | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -Cl)                   | 1491.5          | 6705                            | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                 | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )     | 1026.5          | 9741                            | N-H (3v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping      | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )     | 1459.5          | 6852                            | N-H (2v) asymmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping      | Aromatic amine |
| N-H primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )     | 1502.5          | 6656                            | N-H (2v) symmetric, primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping       | Aromatic amine |
| N-H Amide .NH  | 1570            | 6369                            | N-H (2v), .CONHR  | Amide/protein  |
| N-H Amide .NH or .NH <sub>2</sub>                            | 1460            | 6849                            | N-H (2v), symmetrical   | Urea           |
| N-H Amide .NH or .NH <sub>2</sub>                            | 1463            | 6835                            | N-H (2v), .CONH <sub>2</sub>  | Amide/protein  |
| N-H Amide .NH or .NH <sub>2</sub>                            | 1483            | 6743                            | N-H (2v), .CONH <sub>2</sub>  | Amide/protein  |

(continued)

| In Ascending Alphabetical Functional Group Order (continued)   |                 |                                 |  |   |
|--|-----------------|---------------------------------|--|---|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type                               |
| N-H Amide .NH or .NH <sub>2</sub>  | 1492            | 6702                            | N-H (2v), ArNH <sub>2</sub>  | Amide/protein                               |
| N-H Amide .NH or .NH <sub>2</sub>  | 1500            | 6667                            | N-H (2v), .NH <sub>2</sub>   | Amide/protein                               |
| N-H Amide .NH or .NH <sub>2</sub>  | 1510            | 6623                            | N-H (2v), .CONH <sub>2</sub>   | Amide/protein                               |
| N-H Amide .NH or .NH <sub>2</sub>  | 1520            | 6579                            | N-H (2v), .CONH <sub>2</sub>   | Amide/protein                               |
| N-H Amide .NH or .NH <sub>2</sub>  | 1530            | 6536                            | N-H (2v), RNH <sub>2</sub>   | Amide/protein                               |
| N-H Amide as (.CONH .) & .CONH <sub>2</sub> )  | 2060            | 4854                            | N-H (3d) & N-H stretching combination  | Amides/proteins                             |
| N-H Amide II (.CONH <sub>2</sub> )   | 1980            | 5051                            | N-H stretching (asymmetric) & N-H in-plane bending combination   | Amides/proteins                             |
| N-H Amide with N-R group   | 1471            | 6798                            | N-H (2v), .CONHR   | Amide/protein                               |
| N-H Amide with N-R group   | 1490            | 6711                            | N-H (2v), .CONHR   | Amide/protein                               |
| N-H Amide: (N-H Deformation)   | 2070            | 4831                            | N-H (δ)  | Urea  |
| N-H Amide: NH <sub>2</sub> -C=ONH <sub>2</sub>   | 1990            | 5025                            | N-H stretching & N-H bending combination   | Urea  |
| N-H ammonia in water   | 1534            | 6250                            | N-H (2v) for NH <sub>3</sub> (ammonia) in water  | Ammonia in water                            |
| N-H ammonia in water   | 2000            | 5000                            | N-H (vN-H & δN-H combination) for NH <sub>3</sub> (ammonia) in water   | N-H (combination band) for ammonia in water |
| N-H ammonia in water   | 2210            | 4525                            | N-H (3v) for NH <sub>3</sub> (ammonia) in water  | Ammonia in water                            |
| N-H band found at 4867 cm <sup>-1</sup> for native RNase A shifting to 4878 cm <sup>-1</sup> upon thermal unfolding. | 2053            | 4867–4878                       | N-H from CONH <sub>2</sub> as thermal unfolding of RNase A protein in aqueous solution (assigned to an N-H combination band) | Protein thermal unfolding                   |
| N-H band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | 1470            | 6803                            | N-H (2v) asymmetric stretching from urea   | N-H from urea                               |
| N-H band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | 1485            | 6736                            | N-H (2v) symmetric stretching from urea  | N-H from urea                               |
| N-H bonded combination from polyamide 11   | 1570            | 6368                            | N-H [Bonded NH stretching & 2x amide II deformation (N-H in-plane bending) combination] from polyamide 11                    | Polyamide 11                                |
| N-H bonded from polyamide 11   | 1515            | 6600                            | N-H (2v) stretching bonded NH, disordered phase from polyamide 11  | Polyamide 11                                |
| N-H bonded from polyamide 11   | 1538            | 6500                            | N-H (2v) stretching bonded NH, ordered phase from polyamide 11   | Polyamide 11                                |
| N-H combination band (RNase A) - C=O amide I band  | 2050            | 4878                            | N-H native RNase A combination band at 4867cm <sup>-1</sup> shifting due to thermal unfolding (C=O amide I band).            | N-H from protein                            |
| N-H combination band (RNase A) - C=O amide I band  | 2055            | 4867                            | N-H combination band found in the spectrum of native RNase A (C=O amide I band)  | N-H from protein                            |

| In Ascending Alphabetical Functional Group Order (continued)   |                 |                                 |   |  |
|--|-----------------|---------------------------------|---|--|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type                            |
| N-H combination band from primary amides (R-C=O – NH <sub>2</sub> )  | 1470            | 6805                            | N-H (νN-H asymmetric & νN-H symmetric combination) for primary amides   | N-H combination band from primary amides |
| N-H combination band from primary amides (R-C=O – NH <sub>2</sub> )  | 1960            | 5100                            | N-H [νN-H asymmetric & Amide II deformation (N-H in-plane bending) combination] for primary amides  | N-H combination band from primary amides |
| N-H combination band from secondary amides in native RNase A   | 2075            | 4820                            | N-H [νN-H & amide II deformation (N-H in-plane bending) combination] for secondary amides in native RNase A                                 | N-H from native RNase A                  |
| N-H combination band from secondary amides in proteins   | 2060            | 4850                            | N-H [νN-H & Amide II deformation (N-H in-plane bending) combination] for secondary amides in proteins                                       | N-H from protein                         |
| N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | 1500            | 6666                            | N-H (νN-H asymmetric & νN-H symmetric combination) from urea  | N-H from urea                            |
| N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | 2040            | 4902                            | N-H [νN-H symmetric & Amide II deformation (N-H in-plane bending) combination] for primary amides   | N-H from urea                            |
| N-H combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )   | 2220            | 4505                            | N-H (νN-H asymmetric & NH <sub>2</sub> rocking) combination   | N-H from urea                            |
| N-H combination from polyamide 11  | 2053            | 4870                            | Bonded NH stretching & Amide II (N-H in-plane bending) from polyamide 11  | Polyamide 11                             |
| N-H combination, from primary and secondary aromatic amine (mixtures of aniline and N-ethylaniline in CCl <sub>4</sub> ) | 1972            | 5071                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent from primary and secondary aromatic amines | Primary and secondary aromatic amines    |
| N-H combination, primary aromatic amine ( <i>m</i> -Cl)  | 1968.0          | 5082                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as meta-Cl substituent  | Aromatic amine                           |
| N-H combination, primary aromatic amine ( <i>m</i> -NO <sub>2</sub> )  | 1963.0          | 5095                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as meta-NO <sub>2</sub> substituent                               | Aromatic amine                           |
| N-H combination, primary aromatic amine (no other substituents)  | 1971.5          | 5072                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> no other substituents   | Aromatic amine                           |
| N-H combination, primary aromatic amine ( <i>o</i> -Cl)  | 1971.5          | 5072                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-Cl grouping  | Aromatic amine                           |
| N-H combination, primary aromatic amine ( <i>o</i> -NO <sub>2</sub> )  | 1967.0          | 5084                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-NO <sub>2</sub> substituent                              | Aromatic amine                           |
| (continued)  |                 |                                 |   |  |



| In Ascending Alphabetical Functional Group Order (continued)           |                 |                                 |  |                     |
|--|-----------------|---------------------------------|--|---------------------|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type       |
| N-H combination, primary aromatic amine ( <i>o</i> -OCH <sub>3</sub> ) | 1977.5          | 5057                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as ortho-OCH <sub>3</sub> substituent                    | Aromatic amine      |
| N-H combination, primary aromatic amine ( <i>p</i> -CH <sub>3</sub> )  | 1975.5          | 5062                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-CH <sub>3</sub> grouping                         | Aromatic amine      |
| N-H combination, primary aromatic amine ( <i>p</i> -Cl)                | 1970.5          | 5075                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-Cl substituent                                   | Aromatic amine      |
| N-H combination, primary aromatic amine ( <i>p</i> -NH <sub>2</sub> )  | 1980.5          | 5049                            | N-H (νN-H & δN-H combination), primary aromatic amine in CCl <sub>4</sub> as para-NH <sub>2</sub> grouping                         | Aromatic amine      |
| N-H for secondary amine as (R-NH-R)                                    | 1461            | 6844                            | N-H (2ν), secondary amine as (R-NH-R), indole, first overtone band intensity comparisons, CCl <sub>4</sub> solution                | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1465            | 6826                            | N-H (2ν), secondary amine as (R-NH-R), carbazole, first overtone band intensity comparisons, CCl <sub>4</sub> solution             | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1481            | 6751                            | N-H (2ν), secondary amine as (R-NH-R), N-benzylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution         | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1486            | 6729                            | N-H (2ν), secondary amine as (R-NH-R), diphenylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution         | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1520            | 6580                            | N-H (2ν), secondary amine as (R-NH-R), dimethylamine (vapor), first overtone band intensity comparisons, CCl <sub>4</sub> solution | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1530            | 6536                            | N-H (2ν), secondary amine as (R-NH-R), morpholine, first overtone band intensity comparisons, CCl <sub>4</sub> solution            | N-H secondary amine |
| N-H for secondary amine as (R-NH-R)                                    | 1545            | 6471                            | N-H (2ν), secondary amine as (R-NH-R), diethylamine, first overtone band intensity comparisons, CCl <sub>4</sub> solution          | N-H secondary amine |
| N-H from Gamma-valerolactam  | 2055            | 4865                            | N-H (νN-H & δN-H combination) for gamma-valerolactam   | Gamma-valerolactam  |
| N-H from gamma-valerolactam  | 2090            | 4785                            | N-H [NH stretching & amide II deformation (N-H in-plane bending) combination] for gamma-valerolactam                               | Gamma-valerolactam  |
| N-H from polyamide 11  | 1618            | 6180                            | N-H [4 x Amide II (N-H in-plane bending)] from polyamide 11  | Polyamide 11        |

| In Ascending Alphabetical Functional Group Order (continued)                              |                 |                                 |   |  |
|---|-----------------|---------------------------------|---|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type                            |
| N-H from primary amides (R-C=O – NH <sub>2</sub> )  | 1430            | 6995                            | N-H (2v) symmetric from primary amide (R-C=O – NH <sub>2</sub> )  | N-H from primary amides                  |
| N-H from primary amides (R-C=O – NH <sub>2</sub> )  | 1490            | 6710                            | N-H (2v) asymmetric from primary amide (R-C=O – NH <sub>2</sub> )   | N-H from primary amides                  |
| N-H from secondary amide in proteins  | 1529–1600       | 6540–6250                       | N-H (2v) stretching from secondary amide in proteins  | N-H from protein                         |
| N-H nonbonded from polyamide 11   | 1480            | 6760                            | N-H (2v) stretching non-bonded N-H from Polyamide 11  | Polyamide 11                             |
| N-H primary amine band of diamino compound  | 2205            | 4535                            | N-H (3v) band of primary amine as bisphenol A (I) resins cured with 4,4'-diaminodiphenyl sulfone (II) hardener          | Amine, primary                           |
| N-H Proteins: N-H (3v <sub>B</sub> )  | 2180            | 4587                            | N-H (3d)  | Proteins/amino acids                     |
| N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> )   | 2055            | 4866                            | N-H stretching & C=O stretching (Amide I) combination   | Amides/proteins                          |
| N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> ) from native RNase A                     | 2055            | 4867                            | N-H stretching & C=O stretching (amide I) combination band in the spectrum of native RNase A                            | RNase A                                  |
| N-H/C=O Amide as (.CONH .) & .CONH <sub>2</sub> ) from native RNase A (thermal unfolding) | 2050            | 4878                            | N-H stretching & C=O stretching (amide I) combination band observed in the thermal unfolding observed in native RNase A | RNase A                                  |
| N-H/C=O combination from of native RNase A  | 2024            | 4940                            | N-H/C=O [Bonded NH stretching & amide I (2vC=O stretching) combination] of native RNase A                               | RNase A                                  |
| N-H/C=O combination from polyamide 11   | 2012            | 4970                            | N-H/C=O [Bonded NH stretching & Amide I (2vC=O stretching) combination] from polyamide 11                               | Polyamide 11                             |
| N-H/C=O combination from polyamide 11   | 2127            | 4701                            | N-H/C=O [2 x amide II (N-H in-plane bending) & amide I (2vC=O stretching) combination] from polyamide 11                | Polyamide 11                             |
| N-H/C-N combination band from primary amides (R-C=O – NH <sub>2</sub> )                   | 2010            | 4975                            | N-H [vN-H symmetric & amide III deformation (C-N stretching/N-H in-plane bending) combination] for primary amides       | N-H combination band from primary amides |
| N-H/C-N combination band from primary amides (R-C=O – NH <sub>2</sub> )                   | 2030            | 4925                            | N-H [vN-H asymmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] for primary amides     | N-H combination band from primary amides |
| N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )              | 1990            | 5025                            | N-H [vN-H asymmetric & amide III deformation (C-N stretching/ N-H in-plane bending) combination] for primary amides     | N-H from urea                            |
| (continued)   |                 |                                 |   |  |

| In Ascending Alphabetical Functional Group Order (continued)                     |                     |                                 |  |   |
|--|---------------------|---------------------------------|--|---|
| Functional Group   | Nanometers (nm)     | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type   |
| N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> )     | 2080                | 4808                            | N-H/C-N [ $\nu$ N-H asymmetric & amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea   | N-H/C-N from urea   |
| N-H/C-N from gamma-valerolactam  | 2120                | 4715                            | N-H/C-N [ $\nu$ N-H & amide III deformation (C-N stretching/N-H in-plane bending) combination] for gamma-valerolactam  | Gamma-valerolactam  |
| N-H/C-N/C=O combination band from secondary amides in proteins                   | 2180                | 4590                            | N-H/C-N/C=O [2x amide I (2 $\nu$ C=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for secondary amides in proteins | N-H/C-N/C=O from protein  |
| N-H/C-N/C=O combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> ) | 2180                | 4687                            | N-H/C-N/C=O [2x amide I (2 $\nu$ C=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for urea                         | N-H/C-N/C=O from urea   |
| N-H/C-N/C=O from gamma-valerolactam  | 2145                | 4660                            | N-H/C-N/C=O [2x amide I (2 $\nu$ C=O stretching) & amide III deformation (C-N stretching/N-H in-plane bending) combination] for gamma-valerolactam           | gamma-valerolactam  |
| N-H/C-N/N-H amide II and amide III combination (.CONH .) & .CONH <sub>2</sub> )  | 2050                | 4878                            | N-H in-plane bend & C-N stretching & N-H in-plane bend combination   | Amides/proteins   |
| N-H/C-N/N-H combination from polyamide 11  | 2183                | 4586                            | N-H/C-N/N-H [Bonded NH stretching & amide III (C-N stretching/N-H in-plane bending) combination] from polyamide 11   | Polyamide 11  |
| OH – Classic filter instrument   | 1940                | 5155                            | Classic filter instrument  | Moisture (Classic)  |
| O-H & CH combination from methanol   | 1965                | 5090                            | $\nu$ O-H & $\delta$ C-H combination from CH <sub>3</sub> OH   | Methanol  |
| O-H & C-O stretching and bending combination from methanol                       | 2080                | 4808                            | $\nu$ O-H & $\delta$ O-H combination from CH <sub>3</sub> OH   | Methanol  |
| O-H (.O-H & HOH)   | 1927–1929           | 5189–5184                       | O-H stretching & HOH deformation combination from water molecules in the 3-aminopropyltriethoxysilane-ethanol-water system                                   | O-H stretching & HOH deformation combination from 3-aminopropyltriethoxysilane-ethanol-water system |
| O-H (.O-H & HOH)   | 1930                | 5181                            | O-H stretching & HOH bending combination   | Polysaccharides   |
| O-H (H-O-H) Water  | 1940                | 5155                            | O-H stretching & HOH bending combination   | Water   |
| O-H Alcohol (RO-H)   | 1410                | 7092                            | O-H (2 $\nu$ ), .O-H   | Hydrocarbons, aliphatic   |
| O-H Alcohol O-H with hydrogen bonding  | (1416)<br>1389–1426 | (7060 primarily)<br>7200–7015   | O-H (2 $\nu$ ) from butanol  | Alkyl alcohols (containing one O-H)   |

| In Ascending Alphabetical Functional Group Order (continued)   |                 |                                 |   |  |
|--|-----------------|---------------------------------|---|--|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure   | Material Type                                    |
| O-H Alcohol O-H with hydrogen bonding  | 1460–1603       | 6850–6240                       | O-H (2v) from hydrogen bonded alkyl alcohols as (R-C-OH)  | Alkyl alcohols (containing one O-H)              |
| O-H Alcoholic O-H, intramolecularly bonded   | 1460            | 6850                            | O-H (2v) intra-molecularly bonded from diols  | Alkyl alcohols (diols)                           |
| O-H Alcoholic O-H, nonhydrogen bonded  | 1415            | 7065                            | O-H (2v) nonbonded from diols   | Alkyl alcohols (diols)                           |
| O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>                                       | 513             | 19500                           | O-H (6v) from nonhydrogen bonded short chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH)   | Alkyl alcohols                                   |
| O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>                                       | 599             | 16700                           | O-H (5v) from nonhydrogen bonded short chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH)   | Alkyl alcohols                                   |
| O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>                                       | 741             | 13500                           | O-H (4v) from nonhydrogen bonded short chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH)   | Alkyl alcohols                                   |
| O-H Alkyl alcohols O-H with no hydrogen bonding (R-C-OH) in CCl <sub>4</sub>                                       | 962             | 10400                           | O-H (3v) from nonhydrogen bonded short chain alkyl alcohols in CCl <sub>4</sub> as (R-C-OH)   | Alkyl alcohols                                   |
| O-H Aromatic (ArO-H)   | 1420            | 7042                            | O-H (2v), .O-H  | Hydrocarbons, aromatic                           |
| O-H assigned to molecular water [O-H (.O-H & HOH)]   | 1923            | 5200                            | O-H assigned to molecular water (O-H stretching & HOH deformation combination)  | O-H molecular water                              |
| O-H bound water and the first overtone of an NH stretching mode of the amide groups of ovalbumin                   | 1550            | 6450                            | O-H bound water with several hydrogen bonds and the first overtone of an NH stretching mode of the amide groups of ovalbumin        | O-H bound water of the amide groups of ovalbumin |
| O-H broad band occurring in polyols, alcohols, water, ethylene vinyl alcohols and copolymers containing O-H groups | 1802–2198       | 5550–4550 (broad)               | O-H broad band, due to vO-H & δO-H combination  | Polyols, alcohols, water                         |
| O-H combination band, alcohols or water  | 1065            | 9386                            | 2vO-H & δ C-H methyl combination  | Alcohols as R-C-O-H                              |
| O-H combination band, alcohols or water  | 1580            | 6330                            | 2vO-H , O-H broad band, hydrogen bonded   | Alcohols as R-C-O-H                              |
| O-H deformation band, alcohols or water  | 2096            | 4770                            | 3δ O-H of mid infrared band occurring near 1420 cm <sup>-1</sup>  | Alcohols or water O-H                            |
| O-H stretching band, alkyl alcohols or water   | 1583            | 6319                            | vO-H & δO-H combination reported in the literature from ethylene-vinyl alcohol copolymer spectra, probably better assigned as 2vO-H | Alcohols or water O-H                            |
| O-H stretching band, alcohols or water   | 1408 and 1603   | 7100 and 6240                   | 2vO-H of different aggregates, such as monomers, dimers, and polyols  | Alcohols or water O-H                            |
| (continued)  |                 |                                 |   |  |

| In Ascending Alphabetical Functional Group Order (continued)  |                 |                                 |  |                                |
|---|-----------------|---------------------------------|--|--------------------------------|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type                  |
| O-H from alcohols in CCl <sub>4</sub> (First overtone (2v <sub>s</sub> ) of the O-H alcoholic stretching modes. | 1404–1422       | 7120–7030                       | O-H from alcohols in CCl <sub>4</sub> as n-, sec-, and tert-butanol; the three kinds of alcohols showed an intense band due to the first overtone (2v) of the OH stretching modes  | Alcohols in CCl <sub>4</sub>   |
| O-H from primary alcohols as (-CH <sub>2</sub> -OH)   | 767             | 13038                           | O-H (4v) (-CH <sub>2</sub> -OH), Primary alcohols  | Primary alcohols               |
| O-H from primary alcohols as (-CH <sub>2</sub> -OH)   | 996             | 10040                           | O-H (3v) (-CH <sub>2</sub> -OH), Primary alcohols  | Primary alcohols               |
| O-H from primary alcohols as (-CH <sub>2</sub> -OH)   | 1452            | 6887                            | O-H (2v) (-CH <sub>2</sub> -OH), Primary alcohols  | Primary alcohols               |
| O-H from primary alcohols as (-CH <sub>2</sub> -OH)   | 2740            | 3650                            | O-H (v) (-CH <sub>2</sub> -OH), Primary alcohols   | Primary alcohols               |
| O-H from secondary alcohols as (-CH <sub>2</sub> -OH)   | 773             | 12937                           | O-H (4v) (-CH <sub>2</sub> -OH), Secondary alcohols  | Secondary alcohols             |
| O-H from secondary alcohols as (-CH <sub>2</sub> -OH)   | 1004            | 9960                            | O-H (3v) (-CH <sub>2</sub> -OH), Secondary alcohols  | Secondary alcohols             |
| O-H from secondary alcohols as (-CH <sub>2</sub> -OH)   | 1464            | 6831                            | O-H (2v) (-CH <sub>2</sub> -OH), Secondary alcohols  | Secondary alcohols             |
| O-H from secondary alcohols as (-CH <sub>2</sub> -OH)   | 2762            | 3620                            | O-H (v) (-CH <sub>2</sub> -OH), Secondary alcohols   | Secondary alcohols             |
| O-H from sugar as crystalline sucrose   | 1441            | 6940                            | O-H (2v) carbohydrates (C4 hydroxyl within a crystalline matrix)   | Crystalline sucrose            |
| O-H from tertiary alcohols as (-CH <sub>2</sub> -OH)  | 776             | 12887                           | O-H (4v) (-CH <sub>2</sub> -OH), Tertiary alcohols   | Tertiary alcohols              |
| O-H from tertiary alcohols as (-CH <sub>2</sub> -OH)  | 1006            | 9940                            | O-H (3v) (-CH <sub>2</sub> -OH), Tertiary alcohols   | Tertiary alcohols              |
| O-H from tertiary alcohols as (-CH <sub>2</sub> -OH)  | 1468            | 6812                            | O-H (2v) (-CH <sub>2</sub> -OH), Tertiary alcohols   | Tertiary alcohols              |
| O-H from tertiary alcohols as (-CH <sub>2</sub> -OH)  | 2770            | 3610                            | O-H (v) (-CH <sub>2</sub> -OH), Tertiary alcohols  | Tertiary alcohols              |
| O-H from water  | 1790            | 5587                            | O-H combination  | Water                          |
| O-H from Water at near 0 degrees C  | 770             | 13000                           | O-H (4v) — 3 v <sub>1</sub> + v <sub>3</sub>   | Water                          |
| O-H from water at near 0°C  | 979             | 10210                           | O-H (3v) — 2 v <sub>1</sub> + v <sub>3</sub>   | Water                          |
| O-H from water at near 0°C  | 1200            | 8310                            | O-H, .O-H — v <sub>1</sub> + v <sub>2</sub> + v <sub>3</sub>   | Water                          |
| O-H water at near 0°C   | 1453            | 6880                            | O-H (2v), .O-H   | Water                          |
| O-H water at near 0°C   | 1938            | 5160                            | O-H (2v), .O-H — v <sub>2</sub> + v <sub>3</sub>   | Water                          |
| O-H hydrogen bonding between water and exposed polyvinyl alcohol OH   | 1892            | 5285                            | O-H assigned as a one-to-one hydrogen-bonded to an isolated OH in the manner as OH::OH <sub>2</sub> from the effect of the hydration of the isolated alcohol OH, this pertains to the interactions of water with the OH groups in poly(ethylene-co-vinyl alcohol) (EVOH) | Water and polyvinyl alcohol OH |

| In Ascending Alphabetical Functional Group Order (continued)   |                 |                                 |  |   |
|--|-----------------|---------------------------------|--|---|
| Functional Group   | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type   |
| O-H hydrogen bonding between water and exposed polyvinyl alcohol OH  | 1942            | 5150                            | O-H interaction of multiple hydrogen atoms from poly(ethylene-co-vinyl alcohol) (EVOH) bonded to surrounding associated OH groups (from water) without clustering  | Water and polyvinyl alcohol OH  |
| O-H Hydroxyl O-H free form (not hydrogen bonded)   | 1410            | 7090                            | O-H, free hydroxyl group in dilute CCl <sub>4</sub>  | O-H not hydrogen bonded   |
| O-H Methanol O-H with hydrogen bonding   | 1408            | 7100                            | O-H (2ν) from nonhydrogen bonded methanol in CCl <sub>4</sub> as (CH <sub>3</sub> -OH)   | O-H from Methanol (nonhydrogen bonded)  |
| O-H Methanol O-H with hydrogen bonding   | 1470            | 6800                            | O-H (2ν) from non-hydrogen bonded methanol in CCl <sub>4</sub> as (CH <sub>3</sub> -OH)  | O-H from Methanol (nonhydrogen bonded)  |
| O-H Phenolic O-H   | 1401–1441       | 7140–6940                       | 2νO-H from phenols and aryl alcohols Ar-OH   | Phenolic O-H  |
| O-H phenols, dilute phenol in CCl <sub>4</sub>   | 746 and 782     | 13400 and 12788 (doublet)       | 4νO-H, ortho-iodophenol  | Phenolic O-H  |
| O-H phenols, dilute phenol in CCl <sub>4</sub>   | 755             | 13250                           | 4νO-H dilute phenol in CCl <sub>4</sub>  | Phenolic O-H  |
| O-H phenols, dilute phenol in CCl <sub>4</sub>   | 782 and 746     | 12788 and 13400 (doublet)       | 4νO-H, ortho-iodophenol  | Phenolic O-H  |
| O-H phenols, dilute phenol in CCl <sub>4</sub>   | 1000            | 10000                           | 3νO-H dilute phenol in CCl <sub>4</sub>  | Phenolic O-H  |
| O-H phenols, dilute phenol in CCl <sub>4</sub>   | 1009 and 972    | 9911 and 10288 (doublet)        | 3νO-H, ortho-iodophenol  | Phenolic O-H  |
| O-H phenols, Ortho-substituted halogens  | 1464            | 6830                            | 2νO-H in ortho-substituted halogens on phenols   | Phenolic O-H  |
| O-H Polymeric (.O-H)   | 1450            | 6897                            | O-H (2ν), .O-H   | Starch/polymeric alcohol  |
| O-H Polymeric (.O-H)   | 1490            | 6711                            | O-H (2ν), .O-H   | Starch/polymeric alcohol  |
| O-H Polymeric (.O-H)   | 1540            | 6494                            | O-H (2ν), .O-H   | Starch/polymeric alcohol  |
| O-H Polymeric (.O-H)   | 1960            | 5102                            | O-H stretching & HOH bending combination   | Polysaccharides   |
| O-H Polymeric (.O-H)   | 2090            | 4785                            | O-H combination  | Polymeric .OH   |
| O-H related combination from water change in phase and N-H/C-N combination band from urea (NH <sub>2</sub> -C=O – NH <sub>2</sub> ) from ovalbumin | 2083            | 4800                            | O-H related combination from water change in phase with the increase in protein concentration at pH above 2.8 overlapping with a band representing the N-H/C-N [ν <sub>s</sub> N-H asymmetric & amide III deformation (C-N stretching/N-H in-plane bending) combination] | O-H related combination from water change in phase and N-H/C-N from ovalbumin protein |
| (continued)  |                 |                                 |  |   |

| In Ascending Alphabetical Functional Group Order (continued)  |                 |                                 |  |  |
|---|-----------------|---------------------------------|--|--|
| Functional Group  | Nanometers (nm) | Wavenumbers (cm <sup>-1</sup> ) | Spectra Structure  | Material Type  |
| O-H stretching and bending combination from methanol  | 2016            | 4960                            | $\nu$ O-H & $\delta$ O-H combination from CH <sub>3</sub> OH   | Methanol O-H   |
| O-H stretching vibration ( $\nu$ ) of water molecules in bound-water hydrogen bonding in turquoise minerals   | 3049            | 3280                            | O-H $\nu$ (as intense and very broad band assigned to bound-water hydrogen-bonding in turquoise minerals from Arizona and Senegal with a formula of Cu(Al <sub>6-x</sub> Fe <sub>x</sub> )(PO <sub>4</sub> ) <sub>4</sub> (OH) <sub>8</sub> ·4H <sub>2</sub> O | Bound-water hydrogen bonding in minerals                   |
| O-H stretching vibration ( $\nu$ ) of water molecules in protein-water hydrogen bonding.  | 3067            | 3260                            | O-H $\nu$ (as intense and very broad band assigned to protein-water hydrogen-bonding.  | Protein-water hydrogen bonding.                            |
| O-H stretching vibrations of water molecules in water-water hydrogen bonding.   | 3521            | 2840                            | O-H as intense and very broad band assigned to water-water hydrogen bonding.   | Water-water hydrogen bonding.                              |
| O-H with hydrogen bonding (R-C-OH)  | 1047            | 9550                            | O-H (3 $\nu$ ) from hydrogen bonded short chain alkyl compounds  | Alkyl alcohols   |
| O-H, Monomeric phenol in CCl <sub>4</sub>   | 1420            | 7040                            | 2 $\nu$ O-H monomeric phenol in CCl <sub>4</sub>   |  |
| O-H/C-H Cellulose (.OH & .C-O)  | 2270            | 4405                            | O-H stretching & C-O stretching combination  | Cellulose  |
| O-H/C-H combination   | 1820            | 5495                            | O-H stretching & C-O stretching (3 $\nu_s$ ) combination   | Cellulose  |
| O-H/C-O from glucose  | 2273            | 4400                            | O-H/C-O Glucose absorption from O-H stretching & C-O stretching combination  | Glucose  |
| O-H/C-O Polyfunctional alkyl alcohols   | 1029            | 9720                            | 2 $\nu$ O-H & 3 $\nu$ C-O combination  | Ethers and esters also containing alcohols                 |
| O-H/C-O Polymeric (.O-H & .C-O)   | 2100            | 4762                            | O-H bending & C-O stretching combination   | Polysaccharides (glucose)                                  |
| O-H/C-O stretching combination from methanol  | 2123            | 4710                            | $\nu$ O-H & $\nu$ C-O combination from CH <sub>3</sub> OH  | Methanol O-H   |
| P-OH Phosphate (.P-OH)  | 1908            | 5241                            | O-H (2 $\nu$ ). .P-OH  | Phosphate  |
| Reference – Classic filter instrument   | 1680            | 5952                            | CH – Aromatic used as classic reference filter for filter instruments  | Reference (Classic)  |
| S-H Thiol (.S-H)  | 1740            | 5747                            | S-H (2 $\nu$ ), .S-H   | Thiols   |
| Si-O from silicone  | 1452            | 6887                            | Si-O (2 $\nu$ ) stretch from silicone (dimethyl siloxane)  | Si-O from silicone (dimethyl siloxane)                     |
| Si-O-H stretch + Si-O-Si combination from silicone  | 1933            | 5173                            | Si-O-H stretch + Si-O-Si deformation combination from silicone (dimethyl siloxane)   | Si-O-H stretch + Si-O-Si from silicone (dimethyl siloxane) |
| <i>Notes:</i> 1 $\nu$ , fundamental stretching vibrational absorption band; 2 $\nu$ , first overtone of fundamental stretching band; 3 $\nu$ , second overtone of fundamental stretching band; 4 $\nu$ , third overtone of fundamental stretching band; 5 $\nu$ , fourth overtone of fundamental stretching band; 6 $\nu$ , fifth overtone of fundamental stretching band; 1d, fundamental bending vibrational absorption band; 2d, first overtone of fundamental bending band; 3d, second overtone of fundamental bending band; 4d, third overtone of fundamental bending band; w, deformation (rocking or wagging). |                 |                                 |  |  |





# Appendix E

## Spectra Index by Functional Group or Comparison Series Group

| Functional Group  | Compound Name           | Molecular Formula | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|-------------------|-------------------------|-------------------|------------|---|---|-------------------|
| Alcohol (mono-OH) | 1-Butanol               | C4H10O            | 71-36-3    | 108, 196, 197                             | 154, 198                                  | —                 |
| Alcohol (mono-OH) | 1-Propanol              | C3H8O             | 71-23-8    | 197                                       | —   | —                 |
| Alcohol (mono-OH) | 2-Butanol               | C4H10O            | 78-92-2    | 197                                       | —   | —                 |
| Alcohol (mono-OH) | 2-methyl-2-Propanol     | C4H10O            | 75-65-0    | 108, 197                                  | 154                                       | —                 |
| Alcohol (mono-OH) | 2-Propanol              | C3H8O             | 67-63-0    | 108, 197                                  | 154                                       | —                 |
| Alcohol (mono-OH) | 3-Pentanol              | C5H12O            | 584-02-01  | 108, 197                                  | 154                                       | —                 |
| Alcohol (mono-OH) | Methanol                | CH4O              | 67-56-1    | 108, 196, 197                             | 154, 198                                  | —                 |
| Alcohol (diol)    | 1,2-Ethanediol          | C2H6O2            | 107-21-1   | 109                                       | 155                                       | —                 |
| Alcohol (diol)    | 1,2 Propanediol         | C3H8O2            | 57-55-6    | 109                                       | 155                                       | —                 |
| Alcohol (diol)    | 2,3-Butanediol          | C4H10O2           | 513-85-9   | 109, 196                                  | 155, 198, 199                             | —                 |
| Alcohol (diol)    | 2,4-Pentanediol         | C5H12O2           | 625-69-4   | 109                                       | 155                                       | —                 |
| Alcohol (diol)    | 2,5-Hexanediol          | C6H14O2           | 2935-44-6  | 109                                       | 155                                       | —                 |
| Butanediol series | 1,2-Butanediol          | C4H10O2           | 584-03-2   | 110                                       | 156, 199                                  | —                 |
| Butanediol series | 1,3-Butanediol          | C4H10O2           | 107-88-0   | 110                                       | 156, 199                                  | —                 |
| Butanediol series | 1,4-Butanediol          | C4H10O2           | 110-63-4   | 110                                       | 156, 199                                  | —                 |
| Butanediol series | 2,3-Butanediol          | C4H10O2           | 513-85-9   | 110                                       | 156                                       | —                 |
| Ether             | 1,1,2-trimethoxy-Ethane | C5H12O3           | 24332-20-5 | 111, 200                                  | 157, 201                                  | —                 |
| Ether             | 1,1-dimethoxy-Ethane    | C4H10O2           | 534-15-6   | 111                                       | 157                                       | —                 |
| Ether             | 1,2-diethoxy-Ethane     | C6H14O2           | 629-14-1   | 111                                       | 157                                       | —                 |
| Ether             | 2,2-dimethoxy-Propane   | C5H12O2           | 77-76-9    | 111, 200                                  | 157, 201                                  | —                 |
| Ether             | 2-ethoxy-Ethanol        | C4H10O2           | 110-80-5   | 112                                       | 158                                       | —                 |
| Ether             | 2-phenoxy-Ethanol       | C8H10O2           | 122-99-6   | 112                                       | 158                                       | —                 |
| Ether             | ethoxy-Acetic acid      | C4H8O3            | 627-03-2   | 112                                       | 158                                       | —                 |
| Ether             | ethoxy-Ethene           | C4H8O             | 109-92-2   | 112                                       | 158                                       | —                 |
| Ether             | ethoxy-Ethyne           | C4H6O             | 927-80-0   | 112                                       | 158                                       | —                 |
| Ether             | methoxy-Benzene         | C7H8O             | 100-66-3   | 111, 200                                  | 157, 201                                  | —                 |
| Pentanol series   | 1-Pentanol              | C5H12O            | 71-41-0    | 113                                       | 159                                       | —                 |
| Pentanol series   | 2-Pentanol              | C5H12O            | 6032-29-7  | 113                                       | 159                                       | —                 |
| Pentanol series   | 3-Pentanol              | C5H12O            | 584-02-1   | —   | 159                                       | —                 |
| Pentanol series   | Cyclopentanol           | C5H10O            | 96-41-3    | 113                                       | 159                                       | —                 |
| Pentanol series   | 2-Butene-1,4-diol       | C4H8O2            | 110-64-5   | 113                                       | 159                                       | —                 |
| Pentanol series   | 2-Propene-1-ol          | C3H6O             | 107-18-6   | 113                                       | 159                                       | —                 |
| Aldehyde          | 2-Propynal              | C3H2O             | 624-67-9   | 114                                       | 160                                       | —                 |
| Aldehyde          | Butanal                 | C4H8O             | 123-72-8   | 114, 204                                  | 160, 205                                  | —                 |
| Aldehyde          | Decanal                 | C10H20O           | 112-31-2   | 114, 204                                  | 160, 205                                  | —                 |
| Aldehyde          | Heptanal                | C7H14O            | 111-71-7   | 114, 204                                  | 205                                       | —                 |
| Aldehyde          | Hexanal                 | C6H12O            | 66-25-1    | —   | 160                                       | —                 |

| Functional Group               | Compound Name                | Molecular Formula | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|--------------------------------|------------------------------|-------------------|------------|---|---|-------------------|
| Aldehyde                       | Pentanal                     | C5H10O            | 110-62-3   | 114                                       | 160                                       | —                 |
| Ketone                         | Cyclohexanone                | C6H10O            | 108-94-1   | 115, 202                                  | 161, 203                                  | —                 |
| Ketone                         | 2-Cyclohexen-1-one           | C6H8O             | 930-68-7   | 115                                       | 161                                       | —                 |
| Ketone                         | 2-Hexanone                   | C6H12O            | 591-78-6   | 115                                       | 161                                       | —                 |
| Ketone                         | 2-Propanone (Acetone)        | C3H6O             | 67-64-1    | 115                                       | 161                                       | —                 |
| Ketone                         | 3-Hexanone                   | C6H12O            | 589-38-8   | 115                                       | 161                                       | —                 |
| Ketone                         | 2-Pentanone                  | C5H10O            | 107-87-9   | 202                                       | 203                                       | —                 |
| Ketone                         | 2-Butanone                   | C4H8O             | 78-93-3    | 202                                       | 162, 203                                  | —                 |
| Four-carbon (butyl) comparison | 2-Butanol                    | C4H10O            | 78-92-2    | 116                                       | 162                                       | —                 |
| Four-carbon (butyl) comparison | 2-Butanone                   | C4H8O             | 78-93-3    | 116                                       | —   | —                 |
| Four-carbon (butyl) comparison | 2-ethoxy-Ethanol             | C4H10O2           | 110-80-5   | 116                                       | 162                                       | —                 |
| Four-carbon (butyl) comparison | Butanoic Acid                | C4H8O2            | 107-92-6   | 116                                       | 162                                       | —                 |
| Four-carbon (butyl) comparison | Ethoxy-Ethene                | C4H8O             | 109-92-2   | 116                                       | —   | —                 |
| Four-carbon (butyl) comparison | Ethoxy-Ethyne                | C4H6O             | 927-80-0   | 116                                       | 162                                       | —                 |
| Polyfunctional comparison      | 2-Butenal                    | C4H6O             | 123-73-9   | 117                                       | 163                                       | —                 |
| Polyfunctional comparison      | 2-Furanmethanol              | C5H6O2            | 98-00-0    | 117                                       | 163                                       | —                 |
| Polyfunctional comparison      | 3-methyl-2-Butenal           | C5H8O             | 107-86-8   | 117                                       | 163                                       | —                 |
| Polyfunctional comparison      | 3-phenyl-2-Propenal          | C9H8O             | 14371-10-9 | 117                                       | 163                                       | —                 |
| Polyfunctional comparison      | Benzenepropanal              | C9H10O            | 104-53-0   | 117                                       | 163                                       | —                 |
| Aldehyde, substituted aromatic | 2,4,6-trimethyl-Benzaldehyde | C10H12O           | 487-68-3   | 118                                       | 164                                       | —                 |
| Aldehyde, substituted aromatic | 2,4-dimethyl-Benzaldehyde    | C9H10O            | 15764-16-6 | 118                                       | 164                                       | —                 |
| Aldehyde, substituted aromatic | 2-bromo-Benzaldehyde         | C7H5BrO           | 6630-33-7  | 118                                       | 164                                       | —                 |
| Aldehyde, substituted aromatic | 2-chloro-Benzaldehyde        | C7H5ClO           | 89-98-5    | 118                                       | 164                                       | —                 |
| Aldehyde, substituted aromatic | Benzaldehyde                 | C7H6O             | 100-52-7   | 118                                       | 164                                       | —                 |
| Alkane                         | Methylcyclopentane           | C6H12             | 96-37-7    | 121                                       | —   | —                 |
| Alkane                         | Cycloheptane                 | C7H14             | 291-64-5   | 121                                       | —   | —                 |
| Alkane                         | Cyclohexane                  | C6H12             | 110-82-7   | 121, 206                                  | —   | —                 |
| Alkane                         | Cyclopentane                 | C5H10             | 287-92-3   | 121                                       | —   | —                 |
| Alkane                         | Dodecane                     | C12H26            | 112-40-3   | 119                                       | 165                                       | —                 |
| Alkane                         | Heptane                      | C7H16             | 142-82-5   | —   | 165                                       | —                 |
| Alkane                         | Hexane                       | C6H14             | 110-54-3   | 119                                       | —   | —                 |
| Alkane                         | Octadecane                   | C18H38            | 593-45-3   | 119                                       | 165                                       | —                 |
| Alkane                         | Octane                       | C8H18             | 111-65-9   | 119                                       | 165                                       | —                 |
| Alkane                         | Pentane                      | C5H12             | 109-66-0   | 119                                       | 165                                       | —                 |
| Alkane                         | Undecane                     | C11H24            | 1120-21-4  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Butyl comparison group         | 1-Butanol                    | C4H10O            | 71-36-3    | 120                                       | 166                                       | —                 |
| Butyl comparison group         | 1-Chlorobutane               | C4H9Cl            | 109-69-3   | 120                                       | 166                                       | —                 |

(continued)

| Functional Group                 | Compound Name             | Molecular Formula | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|----------------------------------|---------------------------|-------------------|------------|---|---|-------------------|
| Butyl comparison group           | 2-bromo-Butane            | C4H9Br            | 78-76-2    | 120                                       | 166                                       | —                 |
| Butyl comparison group           | 2-Butanol                 | C4H10O            | 78-92-2    | 120                                       | 166                                       | —                 |
| Butyl comparison group           | 2-chloro-Butane           | C4H9Cl            | 78-86-4    | 120                                       | 166                                       | —                 |
| Butyl comparison group           | 2-iodo-Butane             | C4H9I             | 513-48-4   | 120                                       | 166                                       | —                 |
| Alkane & cycloalkane comparison  | Cycloheptane              | C7H14             | 291-64-5   | 121                                       | 167                                       | —                 |
| Alkane & cycloalkane comparison  | Cyclohexane               | C6H12             | 110-82-7   | 121                                       | 167                                       | —                 |
| Alkane & cycloalkane comparison  | Cyclopentane              | C5H10             | 287-92-3   | 121                                       | 167                                       | —                 |
| Alkane & cycloalkane comparison  | Methylcyclopentane        | C6H12             | 96-37-7    | 121                                       | 167                                       | —                 |
| Ethyl (C2) comparison group      | 1,1,1-trichloro-Ethane    | C2H4Cl3           | 71-55-6    | 122                                       | 168                                       | —                 |
| Ethyl (C2) comparison group      | 1,2-dibromo-Ethane        | C2H4Br2           | 106-93-4   | 122                                       | 168                                       | —                 |
| Ethyl (C2) comparison group      | 1,2-dichloro-Ethane       | C2H4Cl2           | 107-06-2   | 122                                       | 168                                       | —                 |
| Ethyl (C2) comparison group      | 2-bromo-Ethanol           | C2H5BrO           | 540-51-2   | 122                                       | 168                                       | —                 |
| Ethyl (C2) comparison group      | nitro-Ethane              | C2H5NO2           | 79-24-3    | 122                                       | 168                                       | —                 |
| Isomerism comparison group       | 2,2,4-Trimethylpentane    | C8H18             | 540-84-1   | 123, 206                                  | 169, 207                                  | —                 |
| Isomerism comparison group       | 2-Methylpentane           | C6H14             | 107-83-5   | 123                                       | 169                                       | —                 |
| Isomerism comparison group       | Heptane                   | C7H16             | 142-82-5   | 123                                       | 169                                       | —                 |
| Isomerism comparison group       | Pentane                   | C5H12             | 109-66-0   | 123                                       | 169                                       | —                 |
| Methyl comparison group          | Dichloromethyl Silane     | CH4Cl2            | 75-54-7    | 124                                       | 170                                       | —                 |
| Methyl comparison group          | Formic acid, methyl ester | C2H4O2            | 107-31-3   | 124                                       | 170                                       | —                 |
| Methyl comparison group          | Methanol                  | CH4O              | 67-56-1    | 124                                       | 170                                       | —                 |
| Methyl comparison group          | nitro-Methane             | CH3NO2            | 75-52-5    | 124                                       | 170                                       | —                 |
| Propyl comparison group          | 1-chloro-Propane          | C3H7Cl            | 540-54-5   | 125                                       | 171                                       | —                 |
| Propyl comparison group          | 1-Propanol                | C3H8O             | 71-23-8    | 125                                       | 171                                       | —                 |
| Propyl comparison group          | 2-chloro-Propane          | C3H7Cl            | 75-29-6    | 125                                       | 171                                       | —                 |
| Propyl comparison group          | 2-Propanol                | C3H8O             | 67-63-0    | 125                                       | 171                                       | —                 |
| Cycloalkene                      | Cycloheptene              | C7H12             | 628-92-2   | 126                                       | 173                                       | —                 |
| Cycloalkene                      | Cyclohexene               | C6H10             | 110-83-8   | 126                                       | 173                                       | —                 |
| Cycloalkene                      | Cyclooctene               | C8H14             | 931-87-3   | 126                                       | 173                                       | —                 |
| Cycloalkene                      | Cyclopentene              | C5H8              | 142-29-0   | 126                                       | 173                                       | —                 |
| Alkene                           | 1-Decene                  | C10H20            | 872-05-9   | 127, 210                                  | 172, 211                                  | —                 |
| Alkene                           | 1-Heptene                 | C7H14             | 592-76-7   | 210                                       | 211                                       | —                 |
| Alkene                           | 1-Hexene                  | C6H12             | 592-41-6   | 127                                       | 172                                       | —                 |
| Alkene                           | 1-Nonene                  | C9H18             | 124-11-8   | 210                                       | 211                                       | —                 |
| Alkene                           | 1-Octene                  | C8H16             | 111-66-0   | 127                                       | 172                                       | —                 |
| Alkene                           | 1-Pentene                 | C5H10             | 109-67-1   | 127                                       | 172                                       | —                 |
| Alkene                           | 1-Tetradecene             | C14H28            | 1120-36-1  | 127                                       | 172                                       | —                 |
| Alkene, internal versus terminal | 2,3-dimethyl-2-Butene     | C6H12             | 563-79-1   | 128                                       | 174                                       | —                 |
| Alkene, Internal versus terminal | 2-methyl-2-Butene         | C5H10             | 513-35-9   | 128                                       | 174                                       | —                 |
| Alkene, internal versus terminal | 3,3-dimethyl-1-Butene     | C6H12             | 558-37-2   | 128                                       | 174                                       | —                 |

| Functional Group        | Compound Name                                 | Molecular Formula                                | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|-------------------------|---|--|------------|---|---|-------------------|
| Alkyne                  | 1-Heptyne                                     | C <sub>7</sub> H <sub>12</sub>                   | 628-71-7   | 214                                       | 215                                       | —                 |
| Alkyne                  | 1-Octyne                                      | C <sub>8</sub> H <sub>14</sub>                   | 629-05-0   | 129, 214                                  | 175, 215                                  | —                 |
| Alkyne                  | 1-Pentyne                                     | C <sub>5</sub> H <sub>8</sub>                    | 627-19-0   | 129, 214                                  | 175, 215                                  | —                 |
| Alkyne                  | 2-Butyne                                      | C <sub>4</sub> H <sub>6</sub>                    | 503-17-3   | 129                                       | 175                                       | —                 |
| Alkyne                  | 3-chloro-1-Propyne                            | C <sub>3</sub> H <sub>3</sub> Cl                 | 624-65-7   | 129                                       | 175                                       | —                 |
| Alkyne                  | 4-Octyne                                      | C <sub>8</sub> H <sub>14</sub>                   | 1942-45-6  | 129                                       | 175                                       | —                 |
| X-H compound comparison | 1-Butanamine (C-NH)                           | C <sub>4</sub> H <sub>11</sub> N                 | 109-73-9   | 130                                       | 176                                       | —                 |
| X-H compound comparison | 2-Butanethiol (C-SH)                          | C <sub>4</sub> H <sub>10</sub> S                 | 513-53-1   | 130                                       | 176                                       | —                 |
| X-H compound comparison | 2-Butanol (C-OH)                              | C <sub>4</sub> H <sub>10</sub> O                 | 78-92-2    | 130                                       | 176                                       | —                 |
| X-H compound comparison | 2-Propanamine (C-NH)                          | C <sub>3</sub> H <sub>9</sub> N                  | 75-31-0    | 130                                       | 176                                       | —                 |
| X-H compound comparison | Pentane (C-C-H)                               | C <sub>5</sub> H <sub>12</sub>                   | 109-66-0   | 130                                       | 176                                       | —                 |
| Alkyl amine             | 1,2-Propanediamine                            | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub>    | 78-90-0    | 131, 212                                  | 177, 213                                  | —                 |
| Alkyl amine             | 1,7-Heptanediamine                            | C <sub>7</sub> H <sub>18</sub> N <sub>2</sub>    | 646-19-5   | 131                                       | 177                                       | —                 |
| Alkyl amine             | 1-Decanamine                                  | C <sub>10</sub> H <sub>23</sub> N                | 2016-57-1  | 131, 212                                  | 177, 213                                  | —                 |
| Alkyl amine             | Cyclododecanamine                             | C <sub>12</sub> H <sub>25</sub> N                | 1502-03-0  | 131, 212                                  | 177, 213                                  | —                 |
| Alkyl amine             | N,N,N',N'-tetramethyl-1,4-Butanediamine       | C <sub>8</sub> H <sub>20</sub> N <sub>2</sub>    | 111-51-3   | 131                                       | 177                                       | —                 |
| Alkyl amine             | N,N-dipropyl-1-Propanamine                    | C <sub>9</sub> H <sub>21</sub> N                 | 102-69-2   | 131                                       | 177                                       | —                 |
| Aryl amine              | 2-Pyridinemethanol                            | C <sub>6</sub> H <sub>7</sub> NO                 | 586-98-1   | 132                                       | 178                                       | —                 |
| Aryl amine              | 4-methyl-Pyridine                             | C <sub>6</sub> H <sub>7</sub> N                  | 108-89-4   | 132                                       | 178                                       | —                 |
| Aryl amine              | Benzenamine                                   | C <sub>6</sub> H <sub>7</sub> N                  | 62-53-3    | 132                                       | 178                                       | —                 |
| Aryl amine              | Indole, 1-H                                   | C <sub>8</sub> H <sub>7</sub> N                  | 120-72-9   | 132                                       | 178                                       | —                 |
| Aryl amine              | N,N-dimethyl-1,3-Benzenediamine               | C <sub>8</sub> H <sub>12</sub> N <sub>2</sub>    | 2836-04-2  | 132                                       | 178                                       | —                 |
| Amide                   | N-methyl-Acetamide                            | C <sub>3</sub> H <sub>7</sub> NO                 | 79-16-3    | 133, 134, 216                             | 179, 180, 217                             | —                 |
| Amide                   | Formamide                                     | CH <sub>3</sub> NO                               | 75-12-7    | 133, 216                                  | 179, 217                                  | —                 |
| Amide                   | hexamethyl-Phosphoric triamide                | C <sub>6</sub> H <sub>18</sub> N <sub>3</sub> OP | 680-31-9   | 133                                       | 179                                       | —                 |
| Amide                   | N,N-dimethyl-2-Propenamide                    | C <sub>5</sub> H <sub>9</sub> NO                 | 2680-03-7  | 133                                       | 179                                       | —                 |
| Amide                   | N-methyl Propanamide                          | C <sub>4</sub> H <sub>9</sub> NO                 | 1187-58-2  | 134                                       | 180                                       | —                 |
| Amide                   | N, N-diethyl-3-oxo-Butanamide                 | C <sub>6</sub> H <sub>11</sub> NO <sub>2</sub>   | 2044-64-6  | 134                                       | 180                                       | —                 |
| Amide                   | N, N-diethyl-3-methyl-Benzamide               | C <sub>12</sub> H <sub>17</sub> NO               | 134-62-3   | 134                                       | 180                                       | —                 |
| Amide                   | N-methyl Formamide                            | C <sub>2</sub> H <sub>5</sub> NO                 | 123-39-7   | 134                                       | 180                                       | —                 |
| Amino acid              | D-Valine, 3-methyl, 1,1-dimethylethyl ester   | C <sub>10</sub> H <sub>21</sub> NO <sub>2</sub>  | 61169-85-5 | 135                                       | 181                                       | —                 |
| Amino acid              | L-Valine, 3-methyl-, 1,1- dimethylethyl ester | C <sub>10</sub> H <sub>21</sub> NO <sub>2</sub>  | 31556-74-8 | 135                                       | 181                                       | —                 |

(continued)

| Functional Group              | Compound Name                   | Molecular Formula | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|-------------------------------|---------------------------------|-------------------|------------|---|---|-------------------|
| Amino acid                    | N-formyl-Glycine, ethyl ester   | C5H9NO3           | 3154-51-6  | 135                                       | 181                                       | —                 |
| Aromatic compound with N or S | 1-methyl-1H-Pyrrole             | C5H7N             | 96-54-8    | 136                                       | 182                                       | —                 |
| Aromatic compound with N or S | 4-methyl-Pyridine               | C6H7N             | 108-89-4   | 136                                       | 182                                       | —                 |
| Aromatic compound with N or S | Indole, 1H-                     | C8H7N             | 120-72-9   | 136                                       | 182                                       | —                 |
| Aromatic compound with N or S | Quinoline                       | C9H7N             | 91-22-5    | 136                                       | 182                                       | —                 |
| Aromatic compound with N or S | Thiophene                       | C4H4S             | 110-02-1   | 136                                       | 182                                       | —                 |
| Aryl versus alkyl series      | 1,7-Octadiene                   | C8H14             | 3710-30-3  | 137                                       | 183                                       | —                 |
| Aryl versus alkyl series      | 2,2,4-trimethyl-Pentane         | C8H18             | 540-84-1   | 137                                       | 183                                       | —                 |
| Aryl versus alkyl series      | Benzaldehyde                    | C7H6O             | 100-52-7   | 138                                       | 184                                       | —                 |
| Aryl versus alkyl series      | Benzene                         | C6H6              | 71-43-2    | 138, 206, 207                             | 184, 208, 209                             | —                 |
| Aryl versus alkyl series      | Cyclohexane                     | C6H12             | 110-82-7   | 137, 206, 207                             | 183, 208, 209                             | —                 |
| Aryl versus alkyl series      | Cyclohexene                     | C6H10             | 110-83-8   | 137                                       | 183                                       | —                 |
| Aryl versus alkyl series      | methyl-Benzene                  | C7H8              | 108-88-3   | 138                                       | 184                                       | —                 |
| Aryl versus alkyl series      | Octane                          | C8H18             | 111-65-9   | 137, 206, 207                             | 183, 208, 209                             | —                 |
| Aromatic (aryl) compound      | 1,1-Biphenyl                    | C12H10            | 92-52-4    | 139                                       | 185                                       | —                 |
| Aromatic (aryl) compound      | 1,2-dimethyl-Benzene (xylene)   | C8H10             | 95-47-6    | 139                                       | —   | —                 |
| Aromatic (aryl) compound      | 1,3-dimethyl-Benzene (xylene)   | C8H10             | 108-38-3   | —   | 185                                       | —                 |
| Aromatic (aryl) compound      | 1,4-dimethyl-Benzene (xylene)   | C8H10             | 106-42-3   | 139                                       | 185                                       | —                 |
| Aromatic (aryl) compound      | 2,4,5-trichloro-Phenol          | C6H3Cl3O          | 95-95-4    | 139                                       | 185                                       | —                 |
| Aromatic (aryl) compound      | 2-ethyl-Phenol                  | C8H10O            | 90-00-6    | 139                                       | 185                                       | —                 |
| Aromatic (aryl) compound      | 3-methyl-Phenol                 | C7H8O             | 108-39-4   | 139                                       | 185                                       | —                 |
| Aromatic (aryl) compound      | 4-methyl-Phenol                 | C7H8O             | 106-44-5   | 140                                       | 186                                       | —                 |
| Aromatic (aryl) compound      | bromo-Benzene                   | C6H5Br            | 108-86-1   | 140                                       | 186                                       | —                 |
| Aromatic (aryl) compound      | methyl-Benzene                  | C7H8              | 108-88-3   | 140                                       | 186                                       | —                 |
| Aromatic (aryl) compound      | Naphthalene                     | C10H8             | 91-20-3    | 140                                       | 186                                       | —                 |
| Aromatic (aryl) compound      | nitro-Benzene                   | C6H5NO2           | 98-95-3    | 140                                       | 186                                       | —                 |
| Aromatic (aryl) compound      | Phenanthrene                    | C14H10            | 85-01-8    | 140                                       | 186                                       | —                 |
| Cyclic ether                  | 3,4-dihydro-2H-Pyran            | C5H8O             | 110-87-2   | 141                                       | 187                                       | —                 |
| Cyclic ether                  | Furan                           | C4H4O             | 110-00-9   | 141                                       | 187                                       | —                 |
| Cyclic ether                  | tetrahydro-2H-Pyran             | C5H10O            | 142-68-7   | 141                                       | 187                                       | —                 |
| Cyclic ether                  | tetrahydro-4H-Pyran-4-one       | C5H8O2            | 29943-42-8 | 141                                       | 187                                       | —                 |
| Amides, comparison group      | N, N-diethyl-3-methyl-Benzamide | C12H17NO          | 134-62-3   | —   | 180                                       | —                 |
| Amides, comparison group      | N,N-diethyl-3-oxo-Butanamide    | C6H11NO2          | 2044-64-6  | —   | 180                                       | —                 |
| Amides, comparison group      | N-methyl-Acetamide              | C3H7NO            | 79-16-3    | 142                                       | 180, 188                                  | —                 |
| Amides, comparison group      | N-methyl-Formamide              | C2H5NO            | 123-39-7   | —   | 180                                       | —                 |

| Functional Group                    | Compound Name                           | Molecular Formula | CAS Number | 10500–6300 $\text{cm}^{-1}$ (952–1587 nm) | 7200–3800 $\text{cm}^{-1}$ (1389–2632 nm) | Other NIR Regions |
|-------------------------------------|---|-------------------|------------|---|---|-------------------|
| Amides, comparison group            | N-methyl-Propanamide                    | C4H9NO            | 187-58-2   | —   | 180                                       | —                 |
| Acid vs. amide vs. ester comparison | 1-Propen-2-ol acetate                   | C5H8O2            | 108-22-5   | 142                                       | 188                                       | —                 |
| Acid vs. amide vs. ester comparison | 2-ethoxy- acetate-Ethanol               | C6H12O3           | 111-15-9   | 142                                       | 188                                       | —                 |
| Acid vs. amide vs. ester comparison | Acetic acid                             | C4H4O2            | 64-19-7    | 142                                       | 188                                       | —                 |
| Acid vs. amide vs. ester comparison | N-methyl-Acetamide                      | C3H7NO            | 79-16-3    | 142                                       | 188                                       | —                 |
| Carboxylic acid                     | Acetic acid                             | C4H4O2            | 64-19-7    | 218                                       | 219                                       | —                 |
| Carboxylic acid                     | Benzoic acid anhydride                  | C14H10O3          | 93-97-0    | 218                                       | 219                                       | —                 |
| Carboxylic acid                     | Decanoic acid                           | C10H20O2          | 334-48-5   | —   | 219                                       | —                 |
| Carboxylic acid                     | Dodecanoic acid                         | C12H24O2          | 143-07-7   | 143, 218                                  | 189                                       | —                 |
| Carboxylic acid                     | Formic acid                             | CH2O2             | 64-18-6    | 143, 218                                  | 189, 219                                  | —                 |
| Carboxylic acid                     | Methyl ester-Benzoic acid               | C8H8O2            | 93-58-3    | 143                                       | 189                                       | —                 |
| Carboxylic acid                     | Pentanoic acid                          | C5H10O2           | 109-52-4   | —   | —   | —                 |
| Carboxylic acid                     | Propanoic acid                          | C3H6O2            | 79-09-4    | 143                                       | 189                                       | —                 |
| Heterocyclic compound               | 1H-Indole                               | C8H7N             | 120-72-9   | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | 1-methyl-1H-Pyrrole                     | C5H7N             | 96-54-8    | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | 2-bromo-Pyridine                        | C5H4BrN           | 109-04-6   | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | 3-ethyl-Pyridine                        | C7H9N             | 536-78-7   | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | Furan                                   | C4H4O             | 110-00-9   | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | Quinoline                               | C9H7N             | 91-22-5    | 144                                       | 190                                       | —                 |
| Heterocyclic compound               | Thiophene                               | C4H4S             | 110-02-1   | 144                                       | 190                                       | —                 |
| Heterocyclic (5-member ring)        | 2,2-dimethyl-Thiazolidine               | C5H11NS           | 19351-18-9 | 145                                       | 191                                       | —                 |
| Heterocyclic (5-member ring)        | 4,5-dihydro-2-(2-propenylthio)-Thiazole | C6H9NS2           | 3571-74-2  | 145                                       | 191                                       | —                 |
| Heterocyclic (5-member ring)        | 4,5-dihydro-2(methylthio)-Thiazole      | C4H7NS2           | 19975-56-5 | 145                                       | 191                                       | —                 |
| Functional group comparisons        | Undecane                                | C11H24            | 1120-21-4  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional group comparisons        | 1-Decanamine                            | C10H23N           | 2016-57-1  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional group comparisons        | 2,2,4-trimethyl-Pentane                 | C8H18             | 540-84-1   | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional group comparisons        | 2-methyl-2-Propanol                     | C4H10O            | 75-65-0    | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional group comparisons        | 3-Hexanone                              | C6H12O            | 589-38-8   | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional group comparisons        | Benzene                                 | C6H6              | 71-43-2    | 146                                       | 192                                       | —                 |
| Functional group comparisons        | methyl-Benzene                          | C7H8              | 108-88-3   | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |

(continued)





# **Appendix F**

## **Spectra Index by Alpha-Numerical Order of Compound Name**

| Functional Group              | Compound Name                 | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200– 3800 cm <sup>-1</sup><br>(1389– 2632 nm) | Other NIR Regions |
|-------------------------------|-------------------------------|-------------------|------------|--|--|-------------------|
| Ethyl (C2) comparison group   | 1,1,1-trichloro-Ethane        | C2H4Cl2           | 71-55-6    | 122  | 168  | —                 |
| Ether                         | 1,1,2-trimethoxy-Ethane       | C5H12O3           | 24332-20-5 | 111, 200                                       | 157, 201                                       | —                 |
| Aromatic (aryl) compound      | 1,1-Biphenyl                  | C12H10            | 92-52-4    | 139  | 185  | —                 |
| Ether                         | 1,1-dimethoxy-Ethane          | C4H10O2           | 534-15-6   | 111  | 157  | —                 |
| Alcohol (diol)                | 1,2 Propanediol               | C3H8O2            | 57-55-6    | 109  | 155  | —                 |
| Butanediol series             | 1,2-Butanediol                | C4H10O2           | 584-03-2   | 110  | 156, 199                                       | —                 |
| Ethyl (C2) comparison group   | 1,2-dibromo-Ethane            | C2H4Br2           | 106-93-4   | 122  | 168  | —                 |
| Ethyl (C2) comparison group   | 1,2-dichloro-Ethane           | C2H4Cl2           | 107-06-2   | 122  | 168  | —                 |
| Ether                         | 1,2-diethoxy-Ethane           | C6H14O2           | 629-14-1   | 111  | 157  | —                 |
| Aromatic (aryl) compound      | 1,2-dimethyl-Benzene (xylene) | C8H10             | 95-47-6    | 139  | —  | —                 |
| Alcohol (diol)                | 1,2-Ethanediol                | C2H6O2            | 107-21-1   | 109  | 155  | —                 |
| Alkyl amine                   | 1,2-Propanediamine            | C3H10N2           | 78-90-0    | 131, 212                                       | 177, 213                                       | —                 |
| Polyene                       | 1,3,5-Cycloheptatriene        | C7H8              | 544-25-2   | 147  | 193  | —                 |
| Butanediol series             | 1,3-Butanediol                | C4H10O2           | 107-88-0   | 110  | 156, 199                                       | —                 |
| Polyene                       | 1,3-Cyclohexadiene            | C6H8              | 592-57-4   | 147  | 193  | —                 |
| Polyene                       | 1,3-Cyclooctadiene            | C8H12             | 1700-10-3  | 147  | 193  | —                 |
| Aromatic (aryl) compound      | 1,3-dimethyl-Benzene (xylene) | C8H10             | 108-38-3   | —  | 185  | —                 |
| Butanediol series             | 1,4-Butanediol                | C4H10O2           | 110-63-4   | 110  | 156, 199                                       | —                 |
| Aromatic (aryl) compound      | 1,4-dimethyl-Benzene (xylene) | C8H10             | 106-42-3   | 139  | 185  | —                 |
| Polyene                       | 1,5-Hexadiene                 | C6H10             | 592-42-7   | 147, 220                                       | 193, 221                                       | —                 |
| Alkyl amine                   | 1,7-Heptanediamine            | C7H18N2           | 646-19-5   | 131  | 177  | —                 |
| Aryl versus alkyl series      | 1,7-Octadiene                 | C8H14             | 3710-30-3  | 137  | 183  | —                 |
| Polyene                       | 1,7-Octadiene                 | C8H14             | 3710-30-3  | 220  | 221  | —                 |
| X-H compound comparison       | 1-Butanamine (C-NH)           | C4H11N            | 109-73-9   | 130  | 176  | —                 |
| Alcohol (mono-OH)             | 1-Butanol                     | C4H10O            | 71-36-3    | 108, 196, 197                                  | 154, 198                                       | —                 |
| Butyl comparison group        | 1-Butanol                     | C4H10O            | 71-36-3    | 120  | 166  | —                 |
| Butyl comparison group        | 1-chlorobutane                | C4H9Cl            | 109-69-3   | 120  | 166  | —                 |
| Propyl comparison group       | 1-chloro-Propane              | C3H7Cl            | 540-54-5   | 125  | 171  | —                 |
| Alkyl amine                   | 1-Decanamine                  | C10H23N           | 2016-57-1  | 131, 212                                       | 177, 213                                       | —                 |
| Functional group comparisons  | 1-Decanamine                  | C10H23N           | 2016-57-1  | 107, 146, 222, 223                             | 153, 192, 224, 225                             | —                 |
| Alkene                        | 1-Decene                      | C10H20            | 872-05-9   | 127, 210                                       | 172, 211                                       | —                 |
| Alkene                        | 1-Heptene                     | C7H14             | 592-76-7   | 210  | 211  | —                 |
| Alkyne                        | 1-Heptyne                     | C7H12             | 628-71-7   | 214  | 215  | —                 |
| Alkene                        | 1-Hexene                      | C6H12             | 592-41-6   | 127  | 172  | —                 |
| Heterocyclic compound         | 1H-Indole                     | C8H7N             | 120-72-9   | 144  | 190  | —                 |
| Aromatic compound with N or S | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 136  | 182  | —                 |
| Heterocyclic compound         | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 144  | 190  | —                 |

| Functional Group                         | Compound Name                | Molecular Formula                               | CAS Number | 10500 – 6300 cm <sup>-1</sup> (952–1587 nm) | 7200– 3800 cm <sup>-1</sup> (1389– 2632 nm) | Other NIR Regions |
|--|------------------------------|---|------------|---|---|-------------------|
| Alkene                                   | 1-Nonene                     | C <sub>9</sub> H <sub>18</sub>                  | 124-11-8   | 210   | 211   | —                 |
| Alkene                                   | 1-Octene                     | C <sub>8</sub> H <sub>16</sub>                  | 111-66-0   | 127   | 172   | —                 |
| Alkyne                                   | 1-Octyne                     | C <sub>8</sub> H <sub>14</sub>                  | 629-05-0   | 129, 214                                    | 175, 215                                    | —                 |
| Pentanol series                          | 1-Pentanol                   | C <sub>5</sub> H <sub>12</sub> O                | 71-41-0    | 113   | 159   | —                 |
| Alkene                                   | 1-Pentene                    | C <sub>5</sub> H <sub>10</sub>                  | 109-67-1   | 127   | 172   | —                 |
| Alkyne                                   | 1-Pentyne                    | C <sub>5</sub> H <sub>8</sub>                   | 627-19-0   | 129, 214                                    | 175, 215                                    | —                 |
| Alcohol (mono-OH)                        | 1-Propanol                   | C <sub>3</sub> H <sub>8</sub> O                 | 71-23-8    | 197   | —   | —                 |
| Propyl comparison group                  | 1-Propanol                   | C <sub>3</sub> H <sub>8</sub> O                 | 71-23-8    | 125   | 171   | —                 |
| Acid vs. amide vs. ester comparison      | 1-Propen-2-ol acetate        | C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>    | 108-22-5   | 142   | 188   | —                 |
| Alkene                                   | 1-Tetradecene                | C <sub>14</sub> H <sub>28</sub>                 | 1120-36-1  | 127   | 172   | —                 |
| Isomerism comparison group               | 2,2,4-trimethylpentane       | C <sub>8</sub> H <sub>18</sub>                  | 540-84-1   | 123, 206                                    | 169, 207                                    | —                 |
| Aryl vs. alkyl series                    | 2,2,4-trimethyl-Pentane      | C <sub>8</sub> H <sub>18</sub>                  | 540-84-1   | 137   | 183   | —                 |
| Functional group comparisons             | 2,2,4-trimethyl-Pentane      | C <sub>8</sub> H <sub>18</sub>                  | 540-84-1   | 107, 146, 222, 223                          | 153, 192, 224, 225                          | —                 |
| Ether                                    | 2,2-dimethoxy-Propane        | C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>   | 77-76-9    | 111, 200                                    | 157, 201                                    | —                 |
| Heterocyclic (5-member ring)             | 2,2-dimethyl-Thiazolidine    | C <sub>5</sub> H <sub>11</sub> NS               | 19351-18-9 | 145   | 191   | —                 |
| Alcohol (diol)                           | 2,3-Butanediol               | C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>   | 513-85-9   | 109, 196                                    | 155, 198, 199                               | —                 |
| Butanediol series                        | 2,3-Butanediol               | C <sub>4</sub> H <sub>10</sub> O <sub>2</sub>   | 513-85-9   | 110   | 156   | —                 |
| Alkene, internal vs. terminal            | 2,3-dimethyl-2-Butene        | C <sub>6</sub> H <sub>12</sub>                  | 563-79-1   | 128   | 174   | —                 |
| Aromatic (aryl) compound                 | 2,4,5-trichloro-Phenol       | C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub> O | 95-95-4    | 139   | 185   | —                 |
| Aldehyde, substituted aromatic           | 2,4,6-trimethyl-Benzaldehyde | C <sub>10</sub> H <sub>12</sub> O               | 487-68-3   | 118   | 164   | —                 |
| Aldehyde, substituted aromatic           | 2,4-dimethyl-Benzaldehyde    | C <sub>9</sub> H <sub>10</sub> O                | 15764-16-6 | 118   | 164   | —                 |
| Alcohol (diol)                           | 2,4-Pentanediol              | C <sub>5</sub> H <sub>12</sub> O <sub>2</sub>   | 625-69-4   | 109   | 155   | —                 |
| Alcohol (diol)                           | 2,5-Hexanediol               | C <sub>6</sub> H <sub>14</sub> O <sub>2</sub>   | 2935-44-6  | 109   | 155   | —                 |
| Aldehyde, substituted aromatic           | 2-bromo-Benzaldehyde         | C <sub>7</sub> H <sub>5</sub> BrO               | 6630-33-7  | 118   | 164   | —                 |
| Butyl comparison group                   | 2-bromo-Butane               | C <sub>4</sub> H <sub>9</sub> Br                | 78-76-2    | 120   | 166   | —                 |
| Ethyl (C <sub>2</sub> ) comparison group | 2-bromo-Ethanol              | C <sub>2</sub> H <sub>5</sub> BrO               | 540-51-2   | 122   | 168   | —                 |
| Heterocyclic compound                    | 2-bromo-Pyridine             | C <sub>5</sub> H <sub>4</sub> BrN               | 109-04-6   | 144   | 190   | —                 |
| X-H compound comparison                  | 2-Butanethiol (C-SH)         | C <sub>4</sub> H <sub>10</sub> S                | 513-53-1   | 130   | 176   | —                 |
| Alcohol (mono-OH)                        | 2-Butanol                    | C <sub>4</sub> H <sub>10</sub> O                | 78-92-2    | 197   | —   | —                 |
| Four-carbon (butyl) comparison           | 2-Butanol                    | C <sub>4</sub> H <sub>10</sub> O                | 78-92-2    | 116   | 162   | —                 |
| Butyl comparison group                   | 2-Butanol                    | C <sub>4</sub> H <sub>10</sub> O                | 78-92-2    | 120   | 166   | —                 |
| X-H compound comparison                  | 2-Butanol (C-OH)             | C <sub>4</sub> H <sub>10</sub> O                | 78-92-2    | 130   | 176   | —                 |
| Ketone                                   | 2-Butanone                   | C <sub>4</sub> H <sub>8</sub> O                 | 78-93-3    | 202   | 162, 203                                    | —                 |
| Four-carbon (butyl) comparison           | 2-Butanone                   | C <sub>4</sub> H <sub>8</sub> O                 | 78-93-3    | 116   | —   | —                 |
| Polyfunctional comparison                | 2-Butenal                    | C <sub>4</sub> H <sub>6</sub> O                 | 123-73-9   | 117   | 163   | —                 |
| Pentanol series                          | 2-Butene-1,4-diol            | C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>    | 110-64-5   | 113   | 159   | —                 |

(continued)

| Functional Group                    | Compound Name             | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200– 3800 cm <sup>-1</sup><br>(1389– 2632 nm) | Other NIR Regions |
|-------------------------------------|---------------------------|-------------------|------------|--|--|-------------------|
| Alkyne                              | 2-Butyne                  | C4H6              | 503-17-3   | 129  | 175  | —                 |
| Propyl comparison group             | 2-chloro Propane          | C3H7Cl            | 75-29-6    | 125  | 171  | —                 |
| Aldehyde, substituted aromatic      | 2-chloro-Benzaldehyde     | C7H5ClO           | 89-98-5    | 118  | 164  | —                 |
| Butyl comparison group              | 2-chloro-Butane           | C4H9Cl            | 78-86-4    | 120  | 166  | —                 |
| Ketone                              | 2-Cyclohexen-1-one        | C6H8O             | 930-68-7   | 115  | 161  | —                 |
| Acid vs. amide vs. ester comparison | 2-ethoxy- acetate-Ethanol | C6H12O3           | 111-15-9   | 142  | 188  | —                 |
| Ether                               | 2-ethoxy-Ethanol          | C4H10O2           | 110-80-5   | 112  | 158  | —                 |
| Four-carbon (butyl) comparison      | 2-ethoxy-Ethanol          | C4H10O2           | 110-80-5   | 116  | 162  | —                 |
| Aromatic (aryl) compound            | 2-ethyl-Phenol            | C8H10O            | 90-00-6    | 139  | 185  | —                 |
| Polyfunctional comparison           | 2-Furanmethanol           | C5H6O2            | 98-00-0    | 117  | 163  | —                 |
| Ketone                              | 2-Hexanone                | C6H12O            | 591-78-6   | 115  | 161  | —                 |
| Butyl comparison group              | 2-iodo-Butane             | C4H9I             | 513-48-4   | 120  | 166  | —                 |
| Polyene                             | 2-methyl-1,3-Butadiene    | C5H8              | 78-79-5    | 147  | 193  | —                 |
| Alkene, internal vs. terminal       | 2-methyl-2-Butene         | C5H10             | 513-35-9   | 128  | 174  | —                 |
| Alcohol (mono-OH)                   | 2-methyl-2-Propanol       | C4H10O            | 75-65-0    | 108, 197                                       | 154  | —                 |
| Functional group comparisons        | 2-methyl-2-Propanol       | C4H10O            | 75-65-0    | 107, 146, 222, 223                             | 153, 192, 224, 225                             | —                 |
| Isomerism comparison group          | 2-methylpentane           | C6H14             | 107-83-5   | 123  | 169  | —                 |
| Pentanol series                     | 2-Pentanol                | C5H12O            | 6032-29-7  | 113  | 159  | —                 |
| Ketone                              | 2-Pentanone               | C5H10O            | 107-87-9   | 202  | 203  | —                 |
| Ether                               | 2-phenoxy-Ethanol         | C8H10O2           | 122-99-6   | 112  | 158  | —                 |
| X-H compound comparison             | 2-Propanamine (C-NH)      | C3H9N             | 75-31-0    | 130  | 176  | —                 |
| Alcohol (mono-OH)                   | 2-Propanol                | C3H8O             | 67-63-0    | 108, 197                                       | 154  | —                 |
| Propyl comparison group             | 2-Propanol                | C3H8O             | 67-63-0    | 125  | 171  | —                 |
| Ketone                              | 2-Propanone (Acetone)     | C3H6O             | 67-64-1    | 115  | 161  | —                 |
| Pentanol series                     | 2-Propene-1-ol            | C3H6O             | 107-18-6   | 113  | 159  | —                 |
| Aldehyde                            | 2-Propynal                | C3H2O             | 624-67-9   | 114  | 160  | —                 |
| Aryl amine                          | 2-Pyridinemethanol        | C6H7NO            | 586-98-1   | 132  | 178  | —                 |
| Alkene, internal vs. terminal       | 3,3-dimethyl-1-Butene     | C6H12             | 558-37-2   | 128  | 174  | —                 |
| Cyclic ether                        | 3,4-dihydro-2H-Pyran      | C5H8O             | 110-87-2   | 141  | 187  | —                 |
| Alkyne                              | 3-chloro-1-Propyne        | C3H3Cl            | 624-65-7   | 129  | 175  | —                 |
| Heterocyclic compound               | 3-ethyl-Pyridine          | C7H9N             | 536-78-7   | 144  | 190  | —                 |
| Ketone                              | 3-Hexanone                | C6H12O            | 589-38-8   | 115  | 161  | —                 |
| Functional group comparisons        | 3-Hexanone                | C6H12O            | 589-38-8   | 107, 146, 222, 223                             | 153, 192, 224, 225                             | —                 |
| Polyfunctional comparison           | 3-methyl-2-Butenal        | C5H8O             | 107-86-8   | 117  | 163  | —                 |
| Aromatic (aryl) compound            | 3-methyl-Phenol           | C7H8O             | 08-39-4    | 139  | 185  | —                 |
| Alcohol (mono-OH)                   | 3-Pentanol                | C5H12O            | 584-02-01  | 108, 197                                       | 154  | —                 |
| Pentanol series                     | 3-Pentanol                | C5H12O            | 584-02-1   | —  | 159  | —                 |
| Polyfunctional comparison           | 3-phenyl-2-Propenal       | C9H8O             | 14371-10-9 | 117  | 163  | —                 |

| Functional Group                    | Compound Name   | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup> (952–1587 nm) | 7200– 3800 cm <sup>-1</sup> (1389– 2632 nm) | Other NIR Regions |
|-------------------------------------|---|-------------------|------------|---|---|-------------------|
| Heterocyclic (5-member ring)        | 4,5-dihydro-2-(2-propenylthio)-Thiazole                     | C6H9NS2           | 3571-74-2  | 145   | 191   | —                 |
| Heterocyclic (5-member ring)        | 4,5-dihydro-2(methylthio)-Thiazole                          | C4H7NS2           | 19975-56-5 | 145   | 191   | —                 |
| Aromatic (aryl) compound            | 4-methyl-Phenol   | C7H8O             | 106-44-5   | 140   | 186   | —                 |
| Aryl amine                          | 4-methyl-Pyridine   | C6H7N             | 108-89-4   | 132   | 178   | —                 |
| Aromatic compound with N or S       | 4-methyl-Pyridine   | C6H7N             | 108-89-4   | 136   | 182   | —                 |
| Alkyne                              | 4-Octyne  | C8H14             | 1942-45-6  | 129   | 175   | —                 |
| Polymers and elastomers             | 60% polypropylene and 40% polyester                         | Polymer           | N/A        | —   | —   | 148               |
| Polymers and elastomers             | 60% polypropylene-polyethylene acopolymer and 40% polyester | Polymer           | N/A        | —   | —   | 148               |
| Acid vs. amide vs. ester comparison | Acetic acid   | C4H4O2            | 64-19-7    | 142   | 188   | —                 |
| Carboxylic acid                     | Acetic acid   | C4H4O2            | 64-19-7    | 218   | 219   | —                 |
| Third overtone C-H comparison       | Acetone   | C3H6O             | 67-64-1    | —   | —   | 152, 226          |
| Polymers and elastomers             | Atactic polypropylene                                       | Polymer           | N/A        | —   | —   | 148               |
| Aldehyde, substituted aromatic      | Benzaldehyde  | C7H6O             | 100-52-7   | 118   | 164   | —                 |
| Aryl vs. alkyl series               | Benzaldehyde  | C7H6O             | 100-52-7   | 138   | 184   | —                 |
| Aryl amine                          | Benzenamine   | C6H7N             | 62-53-3    | 132   | 178   | —                 |
| Aryl vs. alkyl series               | Benzene   | C6H6              | 71-43-2    | 138, 206, 207                               | 184, 208, 209                               | —                 |
| Functional group comparisons        | Benzene   | C6H6              | 71-43-2    | 146   | 192   | —                 |
| Polyfunctional comparison           | Benzenepropanal   | C9H10O            | 104-53-0   | 117   | 163   | —                 |
| Carboxylic acid                     | Benzoic acid anhydride                                      | C14H10O3          | 93-97-0    | 218   | 219   | —                 |
| Aromatic (aryl) compound            | bromo-Benzene   | C6H5Br            | 108-86-1   | 140   | 186   | —                 |
| Aldehyde                            | Butanal   | C4H8O             | 123-72-8   | 114, 204                                    | 160, 205                                    | —                 |
| Four-carbon (butyl) comparison      | Butanoic acid   | C4H8O2            | 107-92-6   | 116   | 162   | —                 |
| Polymers and elastomers             | Cellulose acetate   | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers             | Cellulose acetate butyrate                                  | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers             | Cellulose propionate  | Polymer           | N/A        | —   | —   | 151               |
| Alkyl amine                         | Cyclododecanamine   | C12H25N           | 1502-03-0  | 131, 212                                    | 177, 213                                    | —                 |
| Alkane                              | Cycloheptane  | C7H14             | 291-64-5   | 121   | —   | —                 |
| Alkane & cycloalkane comparison     | Cycloheptane  | C7H14             | 291-64-5   | 121   | 167   | —                 |
| Cycloalkene                         | Cycloheptene  | C7H12             | 628-92-2   | 126   | 173   | —                 |
| Alkane                              | Cyclohexane   | C6H12             | 110-82-7   | 121, 206                                    | —   | —                 |
| Alkane & cycloalkane comparison     | Cyclohexane   | C6H12             | 110-82-7   | 121   | 167   | —                 |
| Aryl vs. alkyl series               | Cyclohexane   | C6H12             | 110-82-7   | 137, 206, 207                               | 183, 208, 209                               | —                 |
| Ketone                              | Cyclohexanone   | C6H10O            | 108-94-1   | 115, 202                                    | 161, 203                                    | —                 |
| Cycloalkene                         | Cyclohexene   | C6H10             | 110-83-8   | 126   | 173   | —                 |

(continued)

| Functional Group                | Compound Name                                 | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup> (952–1587 nm) | 7200– 3800 cm <sup>-1</sup> (1389– 2632 nm) | Other NIR Regions |
|---------------------------------|---|-------------------|------------|---|---|-------------------|
| Aryl vs. alkyl series           | Cyclohexene                                   | C6H10             | 110-83-8   | 137   | 183   | —                 |
| Cycloalkene                     | Cyclooctene                                   | C8H14             | 931-87-3   | 126   | 173   | —                 |
| Alkane                          | Cyclopentane                                  | C5H10             | 287-92-3   | 121   | —   | —                 |
| Alkane & cycloalkane comparison | Cyclopentane                                  | C5H10             | 287-92-3   | 121   | 167   | —                 |
| Pentanol series                 | Cyclopentanol                                 | C5H10O            | 96-41-3    | 113   | 159   | —                 |
| Cycloalkene                     | Cyclopentene                                  | C5H8              | 142-29-0   | 126   | 173   | —                 |
| Aldehyde                        | Decanal                                       | C10H20O           | 112-31-2   | 114, 204                                    | 160, 205                                    | —                 |
| Carboxylic acid                 | Decanoic acid                                 | C10H20O2          | 334-48-5   | —   | 219   | —                 |
| Methyl comparison group         | dichloromethyl Silane                         | CH4Cl2            | 75-54-7    | 124   | 170   | —                 |
| Alkane                          | Dodecane                                      | C12H26            | 112-40-3   | 119   | 165   | —                 |
| Carboxylic acid                 | Dodecanoic acid                               | C12H24O2          | 143-07-7   | 143, 218                                    | 189   | —                 |
| Amino acid                      | D-Valine, 3-methyl, 1,1-dimethylethyl ester   | C10H21NO2         | 61169-85-5 | 135   | 181   | —                 |
| Ether                           | ethoxy-Acetic acid                            | C4H8O3            | 627-03-2   | 112   | 158   | —                 |
| Ether                           | ethoxy-Ethene                                 | C4H8O             | 109-92-2   | 112   | 158   | —                 |
| Four-carbon (butyl) comparison  | ethoxy-Ethene                                 | C4H8O             | 109-92-2   | 116   | —   | —                 |
| Ether                           | ethoxy-Ethyne                                 | C4H6O             | 927-80-0   | 112   | 158   | —                 |
| Four-carbon (butyl) comparison  | ethoxy-Ethyne                                 | C4H6O             | 927-80-0   | 116   | 162   | —                 |
| Polymers and elastomers         | Ethyl cellulose                               | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers         | Ethylene vinyl acetate                        | Polymer           | N/A        | —   | —   | 148               |
| Amide                           | Formamide                                     | CH3NO             | 75-12-7    | 133, 216                                    | 179, 217                                    | —                 |
| Carboxylic acid                 | Formic acid                                   | CH2O2             | 64-18-6    | 143, 218                                    | 189, 219                                    | —                 |
| Methyl comparison group         | Formic acid, methyl ester                     | C2H4O2            | 107-31-3   | 124   | 170   | —                 |
| Cyclic ether                    | Furan   | C4H4O             | 110-00-9   | 141   | 187   | —                 |
| Heterocyclic compound           | Furan   | C4H4O             | 110-00-9   | 144   | 190   | —                 |
| Aldehyde                        | Heptanal                                      | C7H14O            | 111-71-7   | 114, 204                                    | 205   | —                 |
| Alkane                          | Heptane                                       | C7H16             | 142-82-5   | —   | 165   | —                 |
| Isomerism comparison group      | Heptane                                       | C7H16             | 142-82-5   | 123   | 169   | —                 |
| Amide                           | hexamethyl-Phosphoric triamide                | C6H18N3OP         | 680-31-9   | 133   | 179   | —                 |
| Aldehyde                        | Hexanal                                       | C6H12O            | 66-25-1    | —   | 160   | —                 |
| Alkane                          | Hexane  | C6H14             | 110-54-3   | 119   | —   | —                 |
| Aryl amine                      | Indole, 1-H                                   | C8H7N             | 120-72-9   | 136   | 182   | —                 |
| Aromatic compound with N or S   | Indole, 1H-                                   | C8H7N             | 120-72-9   | 132   | 178   | —                 |
| Amino acid                      | L-Valine, 3-methyl-, 1,1- dimethylethyl ester | C10H21NO2         | 31556-74-8 | 135   | 181   | —                 |
| Alcohol (mono-OH)               | Methanol                                      | CH4O              | 67-56-1    | 108, 196, 197                               | 154, 198                                    | —                 |
| Methyl comparison group         | Methanol                                      | CH4O              | 67-56-1    | 124   | 170   | —                 |
| Ether                           | methoxy-Benzene                               | C7H8O             | 100-66-3   | 111, 200                                    | 157, 201                                    | —                 |
| Carboxylic acid                 | methyl ester-Benzonic acid                    | C8H8O2            | 93-58-3    | 143   | 189   | —                 |

| Functional Group                    | Compound Name                           | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup> (952–1587 nm) | 7200– 3800 cm <sup>-1</sup> (1389– 2632 nm) | Other NIR Regions |
|-------------------------------------|---|-------------------|------------|---|---|-------------------|
| Aryl vs. alkyl series               | methyl-Benzene                          | C7H8              | 108-88-3   | 138   | 184   | —                 |
| Aromatic (aryl) compound            | methyl-Benzene                          | C7H8              | 108-88-3   | 140   | 186   | —                 |
| Functional group comparisons        | methyl-Benzene                          | C7H8              | 108-88-3   | 107, 146, 222, 223                          | 153, 192, 224, 225                          | —                 |
| Alkane                              | Methylcyclopentane                      | C6H12             | 96-37-7    | 121   | —   | —                 |
| Alkane & cycloalkane comparison     | Methylcyclopentane                      | C6H12             | 96-37-7    | 121   | 167   | —                 |
| Amide                               | N,N-dimethyl-3-methyl-Benzamide         | C12H17NO          | 134-62-3   | 134   | 180   | —                 |
| Amide                               | N, N-dimethyl-3-oxo-Butanamide          | C6H11NO2          | 2044-64-6  | 134   | 180   | —                 |
| Alkyl amine                         | N,N,N',N'-tetramethyl-1,4-Butanediamine | C8H20N2           | 111-51-3   | 131   | 177   | —                 |
| Amides, comparison group            | N,N-dimethyl-3-methyl-Benzamide         | C12H17NO          | 134-62-3   | —   | 180   | —                 |
| Aryl amine                          | N,N-dimethyl-1,3-Benzenediamine         | C8H12N2           | 2836-04-2  | —   | 180   | —                 |
| Amide                               | N,N-dimethyl-2-Propenamide              | C5H9NO            | 2680-03-7  | 132   | 178   | —                 |
| Amides, comparison group            | N,N-dimethyl-3-oxo-Butanamide           | C8H15NO2          | 2235-46-3  | 133   | 179   | —                 |
| Alkyl amine                         | N,N-dipropyl-1-Propanamine              | C9H21N            | 102-69-2   | 131   | 177   | —                 |
| Aromatic (aryl) compound            | Naphthalene                             | C10H8             | 91-20-3    | 140   | 186   | —                 |
| Third overtone C-H comparison       | n-Decane                                | C10H22            | 124-18-5   | —   | —   | 152, 226          |
| Amino acid                          | N-formyl-Glycine, ethyl ester           | C5H9NO3           | 3154-51-6  | 135   | 181   | —                 |
| Aromatic (aryl) compound            | nitro-Benzene                           | C6H5NO2           | 98-95-3    | 140   | 186   | —                 |
| Ethyl (C2) comparison group         | nitro-Ethane                            | C2H5NO2           | 79-24-3    | 122   | 168   | —                 |
| Methyl comparison group             | nitro-Methane                           | CH3NO2            | 75-52-5    | 124   | 170   | —                 |
| Amide                               | N-methyl Formamide                      | C2H5NO            | 123-39-7   | 134   | 180   | —                 |
| Amide                               | N-methyl Propanamide                    | C4H9NO            | 1187-58-2  | 134   | 180   | —                 |
| Amide                               | N-methyl-Acetamide                      | C3HH7NO           | 79-16-3    | 133, 134, 216                               | 179, 180, 217                               | —                 |
| Amides, comparison group            | N-methyl-Acetamide                      | C3H7NO            | 79-16-3    | 142   | 180, 188                                    | —                 |
| Acid vs. amide vs. ester comparison | N-methyl-Acetamide                      | C3H7NO            | 79-16-3    | 142   | 188   | —                 |
| Amides, comparison group            | N-methyl-Formamide                      | C2H5NO            | 123-39-7   | —   | 180   | —                 |
| Amides, comparison group            | N-methyl-Propanamide                    | C4H9NO            | 1187-58-2  | —   | 180   | —                 |
| Alkane                              | Octadecane                              | C18H38            | 593-45-3   | 119   | 165   | —                 |
| Alkane                              | Octane                                  | C8H18             | 111-65-9   | 119   | 165   | —                 |
| Aryl vs. alkyl series               | Octane                                  | C8H18             | 111-65-9   | 137, 206, 207                               | 183, 208, 209                               | —                 |

(continued)

| Functional Group              | Compound Name                         | Molecular Formula | CAS Number | 10500 – 6300 cm <sup>-1</sup> (952–1587 nm) | 7200– 3800 cm <sup>-1</sup> (1389– 2632 nm) | Other NIR Regions |
|-------------------------------|---------------------------------------|-------------------|------------|---|---|-------------------|
| Aldehyde                      | Pentanal                              | C5H10O            | 110-62-3   | 114   | 160   | —                 |
| Alkane                        | Pentane                               | C5H12             | 109-66-0   | 119   | 165   | —                 |
| Isomerism comparison group    | Pentane                               | C5H12             | 109-66-0   | 123   | 169   | —                 |
| X-H compound comparison       | Pentane (C-C-H)                       | C5H12             | 109-66-0   | 130   | 176   | —                 |
| Carboxylic acid               | Pentanoic acid                        | C5H10O2           | 109-52-4   | —   | —   | —                 |
| Aromatic (aryl) compound      | Phenanthrene                          | C14H10            | 85-01-8    | 140   | 186   | —                 |
| Polymers and elastomers       | Poly(ethylene oxide)                  | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers       | Poly(isobutyl methacrylate)           | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers       | Poly(vinyl butyral)                   | Polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers       | Poly(vinyl chloride)                  | Polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers       | Poly(vinyl pyrrolidone)               | Polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers       | Poly(vinyl stearate)                  | Polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers       | Poly(vinylidene fluoride)             | Polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers       | Polyacrylic acid                      | Polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers       | Polyethylene, chlorinated (25% Cl)    | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers       | Polypropylene, isotactic, chlorinated | Polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers       | Polystyrene                           | Polymer           | N/A        | —   | —   | 149               |
| Carboxylic acid               | Propanoic acid                        | C3H6O2            | 79-09-4    | 143   | 189   | —                 |
| Aromatic compound with N or S | Quinoline                             | C9H7N             | 91-22-5    | 136   | 182   | —                 |
| Heterocyclic compound         | Quinoline                             | C9H7N             | 91-22-5    | 144   | 190   | —                 |
| Polymers and elastomers       | Silicone                              | Polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers       | Starch                                | Polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers       | Styrene isoprene styrene              | Polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers       | Styrene, ethylene, styrene copolymer  | Polymer           | N/A        | —   | —   | 149               |
| Third overtone C-H comparison | tert-Butanol                          | C4H10O            | 75-65-0    | —   | —   | 152, 226          |
| Cyclic ether                  | tetrahydro-2H-Pyran                   | C5H10O            | 142-68-7   | 141   | 187   | —                 |
| Cyclic ether                  | tetrahydro-4H-Pyran-4-one             | C5H8O2            | 29943-42-8 | 141   | 187   | —                 |
| Aromatic compound with N or S | Thiophene                             | C4H4S             | 110-02-1   | 136   | 182   | —                 |
| Heterocyclic compound         | Thiophene                             | C4H4S             | 110-02-1   | 144   | 190   | —                 |
| Third overtone C-H comparison | Toluene                               | C7H8              | 108-88-3   | —   | —   | 152, 226          |
| Third overtone C-H comparison | Trimethyl pentane                     | C8H18             | 540-84-1   | —   | —   | 152, 226          |
| Alkane                        | Undecane                              | C11H24            | 1120-21-4  | 107, 146, 222, 223                          | 153, 192, 224, 225                          | —                 |
| Functional group comparisons  | Undecane                              | C11H24            | 1120-21-4  | 107, 146, 222, 223                          | 153, 192, 224, 225                          | —                 |

*Note:* N/A indicates natural or synthetic product with no designated CAS number.



# Appendix G

## Spectra Index by Molecular Formula (Carbon Number)

| Functional Group                    | Compound Name             | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup> (952–1587 nm) | 7200–3800 cm <sup>-1</sup> (1389–2632 nm) | Other NIR Regions |
|-------------------------------------|---------------------------|-------------------|------------|---|---|-------------------|
| Carboxylic Acid                     | Formic acid               | CH2O2             | 64-18-6    | 143, 218                                  | 189, 219                                  | —                 |
| Amide                               | Formamide                 | CH3NO             | 75-12-7    | 133, 216                                  | 179, 217                                  | —                 |
| Methyl Comparison Group             | nitro-Methane             | CH3NO2            | 75-52-5    | 124                                       | 170                                       | —                 |
| Methyl Comparison Group             | dichloromethyl Silane     | CH4Cl2            | 75-54-7    | 124                                       | 170                                       | —                 |
| Alcohol (mono-OH)                   | Methanol                  | CH4O              | 67-56-1    | 108, 196, 197                             | 154, 198                                  | —                 |
| Methyl Comparison Group             | Methanol                  | CH4O              | 67-56-1    | 124                                       | 170                                       | —                 |
| Ethyl (C2) Comparison Group         | 1,2-dibromo-Ethane        | C2H4Br2           | 106-93-4   | 122                                       | 168                                       | —                 |
| Ethyl (C2) Comparison Group         | 1,1,1-trichloro-Ethane    | C2H4Cl2           | 71-55-6    | 122                                       | 168                                       | —                 |
| Ethyl (C2) Comparison Group         | 1,2-dichloro-Ethane       | C2H4Cl2           | 107-06-2   | 122                                       | 168                                       | —                 |
| Methyl Comparison Group             | Formic acid, methyl ester | C2H4O2            | 107-31-3   | 124                                       | 170                                       | —                 |
| Ethyl (C2) Comparison Group         | 2-bromo-Ethanol           | C2H5BrO           | 540-51-2   | 122                                       | 168                                       | —                 |
| Amide                               | N-methyl Formamide        | C2H5NO            | 123-39-7   | 134                                       | 180                                       | —                 |
| Amides, Comparison Group            | N-methyl-Formamide        | C2H5NO            | 123-39-7   | —   | 180                                       | —                 |
| Ethyl (C2) Comparison Group         | nitro-Ethane              | C2H5NO2           | 79-24-3    | 122                                       | 168                                       | —                 |
| Alcohol (diol)                      | 1,2-Ethanediol            | C2H6O2            | 107-21-1   | 109                                       | 155                                       | —                 |
| Alkyl Amine                         | 1,2-Propanediamine        | C3H10N2           | 78-90-0    | 131, 212                                  | 177, 213                                  | —                 |
| Aldehyde                            | 2-Propynal                | C3H2O             | 624-67-9   | 114                                       | 160                                       | —                 |
| Alkyne                              | 3-chloro-1-Propyne        | C3H3Cl            | 624-65-7   | 129                                       | 175                                       | —                 |
| Pentanol Series                     | 2-Propene-1-ol            | C3H6O             | 107-18-6   | 113                                       | 159                                       | —                 |
| Ketone                              | 2-Propanone (Acetone)     | C3H6O             | 67-64-1    | 115                                       | 161                                       | —                 |
| Third Overtone C-H Comparison       | Acetone                   | C3H6O             | 67-64-1    | —   | —   | 152, 226          |
| Carboxylic Acid                     | Propanoic acid            | C3H6O2            | 79-09-4    | 143                                       | 189                                       | —                 |
| Propyl Comparison Group             | 1-chloro-Propane          | C3H7Cl            | 540-54-5   | 125                                       | 171                                       | —                 |
| Propyl Comparison Group             | 2-chloro Propane          | C3H7Cl            | 75-29-6    | 125                                       | 171                                       | —                 |
| Amides, Comparison Group            | N-methyl-Acetamide        | C3H7NO            | 79-16-3    | 142                                       | 180, 188                                  | —                 |
| Acid vs. Amide vs. Ester Comparison | N-methyl-Acetamide        | C3H7NO            | 79-16-3    | 142                                       | 188                                       | —                 |
| Alcohol (mono-OH)                   | 1-Propanol                | C3H8O             | 71-23-8    | 197                                       | —   | —                 |
| Alcohol (mono-OH)                   | 2-Propanol                | C3H8O             | 67-63-0    | 108, 197                                  | 154                                       | —                 |
| Propyl Comparison Group             | 1-Propanol                | C3H8O             | 71-23-8    | 125                                       | 171                                       | —                 |
| Propyl Comparison Group             | 2-Propanol                | C3H8O             | 67-63-0    | 125                                       | 171                                       | —                 |
| Alcohol (diol)                      | 1,2 Propanediol           | C3H8O2            | 57-55-6    | 109                                       | 155                                       | —                 |
| X-H Compound Comparison             | 2-Propanamine (C-NH)      | C3H9N             | 75-31-0    | 130                                       | 176                                       | —                 |
| Amide                               | N-methyl-Acetamide        | C3HH7NO           | 79-16-3    | 133, 134, 216                             | 179, 180, 217                             | —                 |
| Alcohol (mono-OH)                   | 1-Butanol                 | C4H10O            | 71-36-3    | 108, 196, 197                             | 154, 198                                  | —                 |
| Alcohol (mono-OH)                   | 2-Butanol                 | C4H10O            | 78-92-2    | 197                                       | —   | —                 |
| Alcohol (mono-OH)                   | 2-methyl-2-Propanol       | C4H10O            | 75-65-0    | 108, 197                                  | 154                                       | —                 |

| Functional Group                    | Compound Name                      | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Other NIR Regions |
|-------------------------------------|------------------------------------|-------------------|------------|--|--|-------------------|
| Four-Carbon (Butyl) Comparison      | 2-Butanol                          | C4H10O            | 78-92-2    | 116  | 162  | —                 |
| Butyl Comparison Group              | 1-Butanol                          | C4H10O            | 71-36-3    | 120  | 166  | —                 |
| Butyl Comparison Group              | 2-Butanol                          | C4H10O            | 78-92-2    | 120  | 166  | —                 |
| X-H Compound Comparison             | 2-Butanol (C-OH)                   | C4H10O            | 78-92-2    | 130  | 176  | —                 |
| Functional Group Comparisons        | 2-methyl-2-Propanol                | C4H10O            | 75-65-0    | 107, 146, 222, 223                           | 153, 192, 224, 225                           | —                 |
| Third Overtone C-H Comparison       | tert-Butanol                       | C4H10O            | 75-65-0    | —  | —  | 152, 226          |
| Alcohol (diol)                      | 2,3-Butanediol                     | C4H10O2           | 513-85-9   | 109, 196                                     | 155, 198, 199                                | —                 |
| Butanediol Series                   | 1,2-Butanediol                     | C4H10O2           | 584-03-2   | 110  | 156, 199                                     | —                 |
| Butanediol Series                   | 1,3-Butanediol                     | C4H10O2           | 107-88-0   | 110  | 156, 199                                     | —                 |
| Butanediol Series                   | 1,4-Butanediol                     | C4H10O2           | 110-63-4   | 110  | 156, 199                                     | —                 |
| Butanediol Series                   | 2,3-Butanediol                     | C4H10O2           | 513-85-9   | 110  | 156  | —                 |
| Ether                               | 1,1-dimethoxy-Ethane               | C4H10O2           | 534-15-6   | 111  | 157  | —                 |
| Ether                               | 2-ethoxy-Ethanol                   | C4H10O2           | 110-80-5   | 112  | 158  | —                 |
| Four-Carbon (Butyl) Comparison      | 2-ethoxy-Ethanol                   | C4H10O2           | 110-80-5   | 116  | 162  | —                 |
| X-H Compound Comparison             | 2-Butanethiol (C-SH)               | C4H10S            | 513-53-1   | 130  | 176  | —                 |
| X-H Compound Comparison             | 1-Butanamine (C-NH)                | C4H11N            | 109-73-9   | 130  | 176  | —                 |
| Cyclic Ether                        | Furan                              | C4H4O             | 110-00-9   | 141  | 187  | —                 |
| Heterocyclic Compound               | Furan                              | C4H4O             | 110-00-9   | 144  | 190  | —                 |
| Acid vs. Amide vs. Ester Comparison | Acetic acid                        | C4H4O2            | 64-19-7    | 142  | 188  | —                 |
| Carboxylic Acid                     | Acetic acid                        | C4H4O2            | 64-19-7    | 218  | 219  | —                 |
| Aromatic Compound with N or S       | Thiophene                          | C4H4S             | 110-02-1   | 136  | 182  | —                 |
| Heterocyclic Compound               | Thiophene                          | C4H4S             | 110-02-1   | 144  | 190  | —                 |
| Alkyne                              | 2-Butyne                           | C4H6              | 503-17-3   | 129  | 175  | —                 |
| Ether                               | ethoxy-Ethyne                      | C4H6O             | 927-80-0   | 112  | 158  | —                 |
| Four-Carbon (Butyl) Comparison      | ethoxy-Ethyne                      | C4H6O             | 927-80-0   | 116  | 162  | —                 |
| Polyfunctional Comparison           | 2-Butenal                          | C4H6O             | 123-73-9   | 117  | 163  | —                 |
| Heterocyclic (5-member ring)        | 4,5-dihydro-2(methylthio)-Thiazole | C4H7NS2           | 19975-56-5 | 145  | 191  | —                 |
| Ether                               | ethoxy-Ethene                      | C4H8O             | 109-92-2   | 112  | 158  | —                 |
| Aldehyde                            | Butanal                            | C4H8O             | 123-72-8   | 114, 204                                     | 160, 205                                     | —                 |
| Ketone                              | 2-Butanone                         | C4H8O             | 78-93-3    | 202  | 162, 203                                     | —                 |
| Four-Carbon (Butyl) Comparison      | 2-Butanone                         | C4H8O             | 78-93-3    | 116  | —  | —                 |
| Four-Carbon (Butyl) Comparison      | Ethoxy-Ethene                      | C4H8O             | 109-92-2   | 116  | —  | —                 |
| Pentanol Series                     | 2-Butene-1,4-diol                  | C4H8O2            | 110-64-5   | 113  | 159  | —                 |
| Four-Carbon (Butyl) Comparison      | Butanoic Acid                      | C4H8O2            | 107-92-6   | 116  | 162  | —                 |
| Ether                               | ethoxy-Acetic acid                 | C4H8O3            | 627-03-2   | 112  | 158  | —                 |

(continued)

| Functional Group                    | Compound Name                 | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Other NIR Regions |
|-------------------------------------|-------------------------------|-------------------|------------|--|--|-------------------|
| Butyl Comparison Group              | 2-bromo-Butane                | C4H9Br            | 78-76-2    | 120  | 166  | —                 |
| Butyl Comparison Group              | 1-chlorobutane                | C4H9Cl            | 109-69-3   | 120  | 166  | —                 |
| Butyl Comparison Group              | 2-chloro-Butane               | C4H9Cl            | 78-86-4    | 120  | 166  | —                 |
| Butyl Comparison Group              | 2-iodo-Butane                 | C4H9I             | 513-48-4   | 120  | 166  | —                 |
| Amide                               | N-methyl Propanamide          | C4H9NO            | 1187-58-2  | 134  | 180  | —                 |
| Amides, Comparison Group            | N-methyl-Propanamide          | C4H9NO            | 1187-58-2  | —  | 180  | —                 |
| Alkane                              | Cyclopentane                  | C5H10             | 287-92-3   | 121  | —  | —                 |
| Alkane & Cycloalkane Comparison     | Cyclopentane                  | C5H10             | 287-92-3   | 121  | 167  | —                 |
| Alkene                              | 1-Pentene                     | C5H10             | 109-67-1   | 127  | 172  | —                 |
| Alkene, Internal versus Terminal    | 2-methyl-2-Butene             | C5H10             | 513-35-9   | 128  | 174  | —                 |
| Pentanol Series                     | Cyclopentanol                 | C5H10O            | 96-41-3    | 113  | 159  | —                 |
| Aldehyde                            | Pentanal                      | C5H10O            | 110-62-3   | 114  | 160  | —                 |
| Ketone                              | 2-Pentanone                   | C5H10O            | 107-87-9   | 202  | 203  | —                 |
| Cyclic Ether                        | tetrahydro-2H-Pyran           | C5H10O            | 142-68-7   | 141  | 187  | —                 |
| Carboxylic Acid                     | Pentanoic acid                | C5H10O2           | 109-52-4   | —  | —  | —                 |
| Heterocyclic (5-member ring)        | 2,2-dimethyl-Thiazolidine     | C5H11NS           | 19351-18-9 | 145  | 191  | —                 |
| Alkane                              | Pentane                       | C5H12             | 109-66-0   | 119  | 165  | —                 |
| Isomerism Comparison Group          | Pentane                       | C5H12             | 109-66-0   | 123  | 169  | —                 |
| X-H Compound Comparison             | Pentane (C-C-H)               | C5H12             | 109-66-0   | 130  | 176  | —                 |
| Alcohol (mono-OH)                   | 3-Pentanol                    | C5H12O            | 584-02-01  | 108, 197                                     | 154  | —                 |
| Pentanol Series                     | 1-Pentanol                    | C5H12O            | 71-41-0    | 113  | 159  | —                 |
| Pentanol Series                     | 2-Pentanol                    | C5H12O            | 6032-29-7  | 113  | 159  | —                 |
| Pentanol Series                     | 3-Pentanol                    | C5H12O            | 584-02-1   | —  | 159  | —                 |
| Alcohol (diol)                      | 2,4-Pentanediol               | C5H12O2           | 625-69-4   | 109  | 155  | —                 |
| Ether                               | 2,2-dimethoxy-Propane         | C5H12O2           | 77-76-7    | 111, 200                                     | 157, 201                                     | —                 |
| Ether                               | 1,1,2-trimethoxy-Ethane       | C5H12O3           | 24332-20-5 | 111, 200                                     | 157, 201                                     | —                 |
| Heterocyclic Compound               | 2-bromo-Pyridine              | C5H4BrN           | 109-04-6   | 144  | 190  | —                 |
| Polyfunctional Comparison           | 2-Furanmethanol               | C5H6O2            | 98-00-0    | 117  | 163  | —                 |
| Aromatic Compound with N or S       | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 136  | 182  | —                 |
| Heterocyclic Compound               | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 144  | 190  | —                 |
| Cycloalkene                         | Cyclopentene                  | C5H8              | 142-29-0   | 126  | 173  | —                 |
| Alkyne                              | 1-Pentyne                     | C5H8              | 627-19-0   | 129, 214                                     | 175, 215                                     | —                 |
| Polyene                             | 2-methyl-1,3-Butadiene        | C5H8              | 78-79-5    | 147  | 193  | —                 |
| Polyfunctional Comparison           | 3-methyl-2-Butenal            | C5H8O             | 107-86-8   | 117  | 163  | —                 |
| Cyclic Ether                        | 3,4-dihydro-2H-Pyran          | C5H8O             | 110-87-2   | 141  | 187  | —                 |
| Cyclic Ether                        | tetrahydro-4H-Pyran-4-one     | C5H8O2            | 29943-42-8 | 141  | 187  | —                 |
| Acid vs. Amide vs. Ester Comparison | 1-Propen-2-ol acetate         | C5H8O2            | 108-22-5   | 142  | 188  | —                 |
| Amide                               | N,N-dimethyl-2-Propenamide    | C5H9NO            | 2680-03-7  | 133  | 179  | —                 |
| Amino Acid                          | N-formyl-Glycine, ethyl ester | C5H9NO3           | 3154-51-6  | 135  | 181  | —                 |

| Functional Group                    | Compound Name                  | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Other NIR Regions |
|-------------------------------------|--------------------------------|-------------------|------------|--|--|-------------------|
| Cycloalkene                         | Cyclohexene                    | C6H10             | 110-83-8   | 126  | 173  | —                 |
| Aryl versus Alkyl Series            | Cyclohexene                    | C6H10             | 110-83-8   | 137  | 183  | —                 |
| Polyene                             | 1,5-Hexadiene                  | C6H10             | 592-42-7   | 147, 220                                     | 193, 221                                     | —                 |
| Ketone                              | Cyclohexanone                  | C6H10O            | 108-94-1   | 115, 202                                     | 161, 203                                     | —                 |
| Amide                               | N, N-dimethyl-3-oxo-Benzamide  | C6H10NO2          | —          | 134  | 180  | —                 |
| Alkane                              | Methylcyclopentane             | C6H12             | 96-37-7    | 121  | —  | —                 |
| Alkane                              | Cyclohexane                    | C6H12             | 110-82-7   | 121, 206                                     | —  | —                 |
| Alkane & Cycloalkane Comparison     | Cyclohexane                    | C6H12             | 110-82-7   | 121  | 167  | —                 |
| Alkane & Cycloalkane Comparison     | methyl-Cyclopentane            | C6H12             | 96-37-7    | 121  | 167  | —                 |
| Alkene                              | 1-Hexene                       | C6H12             | 592-41-6   | 127  | 172  | —                 |
| Alkene, Internal versus Terminal    | 2,3-dimethyl-2-Butene          | C6H12             | 563-79-1   | 128  | 174  | —                 |
| Alkene, Internal versus Terminal    | 3,3-dimethyl-1-Butene          | C6H12             | 558-37-2   | 128  | 174  | —                 |
| Aryl versus Alkyl Series            | Cyclohexane                    | C6H12             | 110-82-7   | 137, 206, 207                                | 183, 208, 209                                | —                 |
| Aldehyde                            | Hexanal                        | C6H12O            | 66-25-1    | —  | 160  | —                 |
| Ketone                              | 2-Hexanone                     | C6H12O            | 591-78-6   | 115  | 161  | —                 |
| Ketone                              | 3-Hexanone                     | C6H12O            | 589-38-8   | 115  | 161  | —                 |
| Functional Group Comparisons        | 3-Hexanone                     | C6H12O            | 589-38-8   | 107, 146, 222, 223                           | 153, 192, 224, 225                           | —                 |
| Acid vs. Amide vs. Ester Comparison | 2-ethoxy- acetate-Ethanol      | C6H12O3           | 111-15-9   | 142  | 188  | —                 |
| Alkane                              | Hexane                         | C6H14             | 110-54-3   | 119  | —  | —                 |
| Isomerism Comparison Group          | 2-methylpentane                | C6H14             | 107-83-5   | 123  | 169  | —                 |
| Alcohol (diol)                      | 2,5-Hexanediol                 | C6H14O2           | 2935-44-6  | 109  | 155  | —                 |
| Ether                               | 1,2-diethoxy-Ethane            | C6H14O2           | 629-14-1   | 111  | 157  | —                 |
| Amide                               | hexamethyl-Phosphoric triamide | C6H18N3OP         | 680-31-9   | 133  | 179  | —                 |
| Aromatic (Aryl) Compound            | 2,4,5-trichloro-Phenol         | C6H3Cl3O          | 95-95-4    | 139  | 185  | —                 |
| Aromatic (Aryl) Compound            | bromo-Benzene                  | C6H5Br            | 108-86-1   | 140  | 186  | —                 |
| Aromatic (Aryl) Compound            | nitro-Benzene                  | C6H5NO2           | 98-95-3    | 140  | 186  | —                 |
| Aryl versus Alkyl Series            | Benzene                        | C6H6              | 71-43-2    | 138, 206, 207                                | 184, 208, 209                                | —                 |
| Functional Group Comparisons        | Benzene                        | C6H6              | 71-43-2    | 146  | 192  | —                 |
| Aryl Amine                          | 4-methyl-Pyridine              | C6H7N             | 108-89-4   | 132  | 178  | —                 |
| Aryl Amine                          | Benzenamine                    | C6H7N             | 62-53-3    | 132  | 178  | —                 |
| Aromatic Compound with N or S       | 4-methyl-Pyridine              | C6H7N             | 108-89-4   | 136  | 182  | —                 |
| Aryl Amine                          | 2-Pyridinemethanol             | C6H7NO            | 586-98-1   | 132  | 178  | —                 |
| Polyene                             | 1,3-Cyclohexadiene             | C6H8              | 592-57-4   | 147  | 193  | —                 |
| Ketone                              | 2-Cyclohexen-1-one             | C6H8O             | 930-68-7   | 115  | 161  | —                 |

(continued)

| Functional Group                | Compound Name                           | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup> (952–1587 nm) | 7200–3800 cm <sup>-1</sup> (1389–2632 nm) | Other NIR Regions |
|---------------------------------|---|-------------------|------------|---|---|-------------------|
| Heterocyclic (5-member ring)    | 4,5-dihydro-2-(2-propenylthio)-Thiazole | C6H9NS2           | 3571-74-2  | 145                                       | 191                                       | —                 |
| Cycloalkene                     | Cycloheptene                            | C7H12             | 628-92-2   | 126                                       | 173                                       | —                 |
| Alkyne                          | 1-Heptyne                               | C7H12             | 628-71-7   | 214                                       | 215                                       | —                 |
| Alkane                          | Cycloheptane                            | C7H14             | 291-64-5   | 121                                       | —   | —                 |
| Alkane & Cycloalkane Comparison | Cycloheptane                            | C7H14             | 291-64-5   | 121                                       | 167                                       | —                 |
| Alkene                          | 1-Heptene                               | C7H14             | 592-76-7   | 210                                       | 211                                       | —                 |
| Aldehyde                        | Heptanal                                | C7H14O            | 111-71-7   | 114, 204                                  | 205                                       | —                 |
| Alkane                          | Heptane                                 | C7H16             | 142-82-5   | —   | 165                                       | —                 |
| Isomerism Comparison Group      | Heptane                                 | C7H16             | 142-82-5   | 123                                       | 169                                       | —                 |
| Alkyl Amine                     | 1,7-Heptanediamine                      | C7H18N2           | 646-19-5   | 131                                       | 177                                       | —                 |
| Aldehyde, Substituted Aromatic  | 2-bromo-Benzaldehyde                    | C7H5BrO           | 6630-33-7  | 118                                       | 164                                       | —                 |
| Aldehyde, Substituted Aromatic  | 2-chloro-Benzaldehyde                   | C7H5ClO           | 89-98-5    | 118                                       | 164                                       | —                 |
| Aldehyde, Substituted Aromatic  | Benzaldehyde                            | C7H6O             | 100-52-7   | 118                                       | 164                                       | —                 |
| Aryl versus Alkyl Series        | Benzaldehyde                            | C7H6O             | 100-52-7   | 138                                       | 184                                       | —                 |
| Aryl versus Alkyl Series        | methyl-Benzene                          | C7H8              | 108-88-3   | 138                                       | 184                                       | —                 |
| Aromatic (Aryl) Compound        | methyl-Benzene                          | C7H8              | 108-88-3   | 140                                       | 186                                       | —                 |
| Functional Group Comparisons    | methyl-Benzene                          | C7H8              | 108-88-3   | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Polyene                         | 1,3,5-Cycloheptatriene                  | C7H8              | 544-25-2   | 147                                       | 193                                       | —                 |
| Third Overtone C-H Comparison   | Toluene                                 | C7H8              | 108-88-3   | —   | —   | 152, 226          |
| Ether                           | methoxy-Benzene                         | C7H8O             | 100-66-3   | 111, 200                                  | 157, 201                                  | —                 |
| Aromatic (Aryl) Compound        | 3-methyl-Phenol                         | C7H8O             | 108-39-4   | 139                                       | 185                                       | —                 |
| Aromatic (Aryl) Compound        | 4-methyl-Phenol                         | C7H8O             | 106-44-5   | 140                                       | 186                                       | —                 |
| Heterocyclic Compound           | 3-ethyl-Pyridine                        | C7H9N             | 536-78-7   | 144                                       | 190                                       | —                 |
| Aromatic (Aryl) Compound        | 1,2-dimethyl-Benzene (xylene)           | C8H10             | 95-47-6    | 139                                       | —   | —                 |
| Aromatic (Aryl) Compound        | 1,3-dimethyl-Benzene (xylene)           | C8H10             | 108-38-3   | —   | 185                                       | —                 |
| Aromatic (Aryl) Compound        | 1,4-dimethyl-Benzene (xylene)           | C8H10             | 106-42-3   | 139                                       | 185                                       | —                 |
| Aromatic (Aryl) Compound        | 2-ethyl-Phenol                          | C8H10O            | 90-00-6    | 139                                       | 185                                       | —                 |
| Ether                           | 2-phenoxy-Ethanol                       | C8H10O2           | 122-99-6   | 112                                       | 158                                       | —                 |
| Polyene                         | 1,3-Cyclooctadiene                      | C8H12             | 1700-10-3  | 147                                       | 193                                       | —                 |
| Aryl Amine                      | N,N-dimethyl-1,3-Benzenediamine         | C8H12N2           | 2836-04-2  | 132                                       | 178                                       | —                 |
| Cycloalkene                     | Cyclooctene                             | C8H14             | 931-87-3   | 126                                       | 173                                       | —                 |
| Alkyne                          | 1-Octyne                                | C8H14             | 629-05-0   | 129, 214                                  | 175, 215                                  | —                 |
| Alkyne                          | 4-Octyne                                | C8H14             | 1942-45-6  | 129                                       | 175                                       | —                 |
| Aryl versus Alkyl Series        | 1,7-Octadiene                           | C8H14             | 3710-30-3  | 137                                       | 183                                       | —                 |

| Functional Group               | Compound Name                                 | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Other NIR Regions |
|--------------------------------|---|-------------------|------------|--|--|-------------------|
| Polyene                        | 1,7-Octadiene                                 | C8H14             | 3710-30-3  | 220  | 221  | —                 |
| Amides, Comparison Group       | N,N-diethyl-3-oxo-Butanamide                  | C8H15NO2          | 2235-46-3  | —  | 180  | —                 |
| Alkene                         | 1-Octene                                      | C8H16             | 111-66-0   | 127  | 172  | —                 |
| Alkane                         | Octane  | C8H18             | 111-65-9   | 119  | 165  | —                 |
| Isomerism Comparison Group     | 2,2,4-trimethylpentane                        | C8H18             | 540-84-1   | 123, 206                                     | 169, 207                                     | —                 |
| Aryl versus Alkyl Series       | 2,2,4-trimethyl-Pentane                       | C8H18             | 540-84-1   | 137  | 183  | —                 |
| Aryl versus Alkyl Series       | Octane  | C8H18             | 111-65-9   | 137, 206, 207                                | 183, 208, 209                                | —                 |
| Functional Group Comparisons   | 2,2,4-trimethyl-Pentane                       | C8H18             | 540-84-1   | 107, 146, 222, 223                           | 153, 192, 224, 225                           | —                 |
| Third Overtone C-H Comparison  | Trimethyl pentane                             | C8H18             | 540-84-1   | —  | —  | 152, 226          |
| Alkyl Amine                    | N,N,N',N'-tetramethyl-1,4-Butanediamine       | C8H20N2           | 111-51-3   | 131  | 177  | —                 |
| Aryl Amine                     | Indole, 1-H                                   | C8H7N             | 120-72-9   | 132  | 178  | —                 |
| Aromatic Compound with N or S  | Indole, 1H-                                   | C8H7N             | 120-72-9   | 136  | 182  | —                 |
| Heterocyclic Compound          | 1H-Indole                                     | C8H7N             | 120-72-9   | 144  | 190  | —                 |
| Carboxylic Acid                | Methyl ester-Benzoic acid                     | C8H8O2            | 93-58-3    | 143  | 189  | —                 |
| Polyfunctional Comparison      | Benzenepropanal                               | C9H10O            | 104-53-0   | 117  | 163  | —                 |
| Aldehyde, Substituted Aromatic | 2,4-dimethyl-Benzaldehyde                     | C9H10O            | 15764-16-6 | 118  | 164  | —                 |
| Alkene                         | 1-Nonene                                      | C9H18             | 124-11-8   | 210  | 211  | —                 |
| Alkyl Amine                    | N,N-dipropyl-1-Propanamine                    | C9H21N            | 102-69-2   | 131  | 177  | —                 |
| Aromatic Compound with N or S  | Quinoline                                     | C9H7N             | 91-22-5    | 136  | 182  | —                 |
| Heterocyclic Compound          | Quinoline                                     | C9H7N             | 91-22-5    | 144  | 190  | —                 |
| Polyfunctional Comparison      | 3-phenyl-2-Propenal                           | C9H8O             | 14371-10-9 | 117  | 163  | —                 |
| Aldehyde, Substituted Aromatic | 2,4,6-trimethyl-Benzaldehyde                  | C10H12O           | 487-68-3   | 118  | 164  | —                 |
| Amide                          | N, N-dimethyl-3-methyl-Benzamide              | C10H13NO          | —          | 134  | 180  | —                 |
| Alkene                         | 1-Decene                                      | C10H20            | 872-05-9   | 127, 210                                     | 172, 211                                     | —                 |
| Aldehyde                       | Decanal                                       | C10H20O           | 112-31-2   | 114, 204                                     | 160, 205                                     | —                 |
| Carboxylic Acid                | Decanoic acid                                 | C10H20O2          | 334-48-5   | —  | 219  | —                 |
| Amino Acid                     | D-Valine, 3-methyl, 1,1-dimethylethyl ester   | C10H21NO2         | 61169-85-5 | 135  | 181  | —                 |
| Amino Acid                     | L-Valine, 3-methyl-, 1,1- dimethylethyl ester | C10H21NO2         | 31556-74-8 | 135  | 181  | —                 |
| Third Overtone C-H Comparison  | n-Decane                                      | C10H22            | 124-18-5   | —  | —  | 152, 226          |
| Alkyl Amine                    | 1-Decanamine                                  | C10H23N           | 2016-57-1  | 131, 212                                     | 177, 213                                     | —                 |

(continued)

| Functional Group             | Compound Name   | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup> (952–1587 nm) | 7200–3800 cm <sup>-1</sup> (1389–2632 nm) | Other NIR Regions |
|------------------------------|---|-------------------|------------|---|---|-------------------|
| Functional Group Comparisons | 1-Decanamine  | C10H23N           | 2016-57-1  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Aromatic (Aryl) Compound     | Naphthalene   | C10H8             | 91-20-3    | 140                                       | 186                                       | —                 |
| Alkane                       | Undecane  | C11H24            | 1120-21-4  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Functional Group Comparisons | Undecane  | C11H24            | 1120-21-4  | 107, 146, 222, 223                        | 153, 192, 224, 225                        | —                 |
| Aromatic (Aryl) Compound     | 1,1-Biphenyl  | C12H10            | 92-52-4    | 139                                       | 185                                       | —                 |
| Amides, Comparison Group     | N,N-diethyl-3-methyl-Benzamide                              | C12H17NO          | 134-62-3   | —   | 180                                       | —                 |
| Carboxylic Acid              | Dodecanoic acid   | C12H24O2          | 143-07-7   | 143, 218                                  | 189                                       | —                 |
| Alkyl Amine                  | Cyclododecanamine   | C12H25N           | 1502-03-0  | 131, 212                                  | 177, 213                                  | —                 |
| Alkane                       | Dodecane  | C12H26            | 112-40-3   | 119                                       | 165                                       | —                 |
| Aromatic (Aryl) Compound     | Phenanthrene  | C14H10            | 85-01-8    | 140                                       | 186                                       | —                 |
| Carboxylic Acid              | Benzoic acid anhydride                                      | C14H10O3          | 93-97-0    | 218                                       | 219                                       | —                 |
| Alkene                       | 1-Tetradecene   | C14H28            | 1120-36-1  | 127                                       | 172                                       | —                 |
| Alkane                       | Octadecane  | C18H38            | 593-45-3   | 119                                       | 165                                       | —                 |
| Polymers and elastomers      | 60% polypropylene and 40% polyester                         | polymer           | N/A        | —   | —   | 148               |
| Polymers and elastomers      | 60% polypropylene-polyethylene acopolymer and 40% polyester | polymer           | N/A        | —   | —   | 148               |
| Polymers and elastomers      | Atactic Polypropylene                                       | polymer           | N/A        | —   | —   | 148               |
| Polymers and elastomers      | Cellulose acetate   | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Cellulose acetate butyrate                                  | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Cellulose propionate  | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Ethyl cellulose   | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Ethylene Vinyl Acetate                                      | polymer           | N/A        | —   | —   | 148               |
| Polymers and elastomers      | Poly(ethylene oxide)  | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Poly(isobutyl methacrylate)                                 | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Poly(vinyl butyral)   | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Poly(vinyl chloride)  | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Poly(vinyl pyrrolidone)                                     | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Poly(vinyl stearate)  | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Poly(vinylidene fluoride)                                   | polymer           | N/A        | —   | —   | 151               |
| Polymers and elastomers      | Polyacrylic acid  | polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers      | Polyethylene, chlorinated (25% Cl)                          | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Polypropylene, isotactic, chlorinated                       | polymer           | N/A        | —   | —   | 150               |
| Polymers and elastomers      | Polystyrene   | polymer           | N/A        | —   | —   | 149               |
| Polymers and elastomers      | Silicone  | polymer           | N/A        | —   | —   | 149               |







# Appendix H

## **Spectra Index Alphabetical by Molecular Formula with Structural Formula Given**

| Functional Group                         | Compound Name             | Molecular Formula                             | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula  |
|--|---------------------------|---|------------|--|--|---|
| Carboxylic acid                          | Formic acid               | CH <sub>2</sub> O <sub>2</sub>                | 64-18-6    | 143, 218                                     | 189, 219                                     | HCOOH   |
| Amide                                    | Formamide                 | CH <sub>3</sub> NO                            | 75-12-7    | 133, 216                                     | 179, 217                                     | HCONH <sub>2</sub>  |
| Methyl comparison group                  | nitro-Methane             | CH <sub>3</sub> NO <sub>2</sub>               | 75-52-5    | 124  | 170  | H <sub>3</sub> CNO <sub>2</sub>   |
| Methyl comparison group                  | dichloromethyl Silane     | CH <sub>4</sub> Cl <sub>2</sub>               | 75-54-7    | 124  | 170  | H <sub>3</sub> SiCl <sub>2</sub> H  |
| Alcohol (mono-OH)                        | Methanol                  | CH <sub>4</sub> O                             | 67-56-1    | 108, 196, 197                                | 154, 198                                     | H <sub>3</sub> COH  |
| Methyl comparison group                  | Methanol                  | CH <sub>4</sub> O                             | 67-56-1    | 124  | 170  | H <sub>3</sub> COH  |
| Ethyl (C <sub>2</sub> ) comparison group | 1,2-dibromo-Ethane        | C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> | 106-93-4   | 122  | 168  | BrH <sub>2</sub> CCH <sub>2</sub> Br  |
| Ethyl (C <sub>2</sub> ) comparison group | 1,1,1-trichloro-Ethane    | C <sub>2</sub> H <sub>4</sub> Cl <sub>3</sub> | 71-55-6    | 122  | 168  | H <sub>3</sub> CCCl <sub>3</sub>  |
| Ethyl (C <sub>2</sub> ) comparison group | 1,2-dichloro-Ethane       | C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> | 107-06-2   | 122  | 168  | H <sub>3</sub> CCHCl <sub>2</sub>   |
| Methyl comparison group                  | Formic acid, methyl ester | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>  | 107-31-3   | 124  | 170  | HCOOCH <sub>3</sub>   |
| Ethyl (C <sub>2</sub> ) comparison group | 2-bromo-Ethanol           | C <sub>2</sub> H <sub>5</sub> BrO             | 540-51-2   | 122  | 168  | HOCH <sub>2</sub> CH <sub>2</sub> Br  |
| Amide                                    | N-methyl-Formamide        | C <sub>2</sub> H <sub>5</sub> NO              | 123-39-7   | 134  | 180  | HCONHCH <sub>3</sub>  |
| Amides, comparison group                 | N-methyl-Formamide        | C <sub>2</sub> H <sub>5</sub> NO              | 123-39-7   | —  | 180  | HCONHCH <sub>3</sub>  |
| Ethyl (C <sub>2</sub> ) comparison group | nitro-Ethane              | C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub> | 79-24-3    | 122  | 168  | H <sub>3</sub> CCH <sub>2</sub> NO <sub>2</sub>                                 |
| Alcohol (diol)                           | 1,2-Ethanediol            | C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>  | 107-21-1   | 109  | 155  | HOCH <sub>2</sub> CH <sub>2</sub> OH  |
| Alkyl amine                              | 1,2-Propanediamine        | C <sub>3</sub> H <sub>10</sub> N <sub>2</sub> | 78-90-0    | 131, 212                                     | 177, 213                                     | H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> |
| Aldehyde                                 | 2-Propynal                | C <sub>3</sub> H <sub>2</sub> O               | 624-67-9   | 114  | 160  | HCCCHO  |
| Alkyne                                   | 3-chloro-1-Propyne        | C <sub>3</sub> H <sub>3</sub> Cl              | 624-65-7   | 129  | 175  | HCCCH <sub>2</sub> Cl   |
| Ketone                                   | 2-Propanone (Acetone)     | C <sub>3</sub> H <sub>6</sub> O               | 67-64-1    | 115  | 161  | H <sub>3</sub> CCOCH <sub>3</sub>   |
| Pentanol series                          | 2-Propene-1-ol            | C <sub>3</sub> H <sub>6</sub> O               | 107-18-6   | 113  | 159  | H <sub>2</sub> CCHCH <sub>2</sub> OH  |
| Third overtone C-H comparison            | Acetone                   | C <sub>3</sub> H <sub>6</sub> O               | 67-64-1    | —  | —  | H <sub>3</sub> CCOCH <sub>3</sub>   |
| Carboxylic acid                          | Propanoic acid            | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>  | 79-09-4    | 143  | 189  | H <sub>3</sub> CCH <sub>2</sub> COOH  |
| Propyl comparison group                  | 1-chloro-Propane          | C <sub>3</sub> H <sub>7</sub> Cl              | 540-54-5   | 125  | 171  | H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> Cl                              |
| Propyl comparison group                  | 2-chloro Propane          | C <sub>3</sub> H <sub>7</sub> Cl              | 75-29-6    | 125  | 171  | H <sub>3</sub> CCHClCH <sub>3</sub>   |
| Amides, comparison group                 | N-methyl-Acetamide        | C <sub>3</sub> H <sub>7</sub> NO              | 79-16-3    | 142  | 180, 188                                     | H <sub>3</sub> CNHCOCH <sub>3</sub>   |
| Acid vs. amide vs. ester                 | N-methyl-Acetamide        | C <sub>3</sub> H <sub>7</sub> NO              | 79-16-3    | 142  | 188  | H <sub>3</sub> CNHCOCH <sub>3</sub>   |
| Alcohol (mono-OH)                        | 1-Propanol                | C <sub>3</sub> H <sub>8</sub> O               | 71-23-8    | 197  | —  | H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> OH                              |
| Propyl comparison group                  | 1-Propanol                | C <sub>3</sub> H <sub>8</sub> O               | 71-23-8    | 125  | 171  | H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> OH                              |
| Alcohol (mono-OH)                        | 2-Propanol                | C <sub>3</sub> H <sub>8</sub> O               | 67-63-0    | 108, 197                                     | 154  | H <sub>3</sub> CCHOHCH <sub>3</sub>   |
| Propyl comparison group                  | 2-Propanol                | C <sub>3</sub> H <sub>8</sub> O               | 67-63-0    | 125  | 171  | H <sub>3</sub> CCHOHCH <sub>3</sub>   |
| Alcohol (diol)                           | 1,2 Propanediol           | C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>  | 57-55-6    | 109  | 155  | HOCH <sub>2</sub> CHOHCH <sub>3</sub>   |
| X-H compound comparison                  | 2-Propanamine (C-NH)      | C <sub>3</sub> H <sub>9</sub> N               | 75-31-0    | 130  | 176  | H <sub>3</sub> CCHCH <sub>3</sub> NH <sub>2</sub>                               |
| Amide                                    | N-methyl-Acetamide        | C <sub>3</sub> HH <sub>7</sub> NO             | 79-16-3    | 133, 134, 216                                | 179, 180, 217                                | H <sub>3</sub> NHCOCH <sub>3</sub>  |
| Alcohol (mono-OH)                        | 1-Butanol                 | C <sub>4</sub> H <sub>10</sub> O              | 71-36-3    | 108, 196, 197                                | 154, 198                                     | H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH              |
| Butyl comparison group                   | 1-Butanol                 | C <sub>4</sub> H <sub>10</sub> O              | 71-36-3    | 120  | 166  | H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH              |

| Functional Group                    | Compound Name                      | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula |
|-------------------------------------|------------------------------------|-------------------|------------|--|--|--------------------|
| Alcohol (mono-OH)                   | 2-Butanol                          | C4H10O            | 78-92-2    | 197  | —  | H3CCHOHCH2CH2      |
| Four-carbon (butyl) comparison      | 2-Butanol                          | C4H10O            | 78-92-2    | 116  | 162  | H3CCHOHCH2CH2      |
| Butyl comparison group              | 2-Butanol                          | C4H10O            | 78-92-2    | 120  | 166  | H3CCHOHCH2CH2      |
| X-H compound comparison             | 2-Butanol (C-OH)                   | C4H10O            | 78-92-2    | 130  | 176  | H3CCHOHCH2CH2      |
| Alcohol (mono-OH)                   | 2-methyl-2-Propanol                | C4H10O            | 75-65-0    | 108, 197                                     | 154  | H3CCCH3CH3OH       |
| Functional group comparisons        | 2-methyl-2-Propanol                | C4H10O            | 75-65-0    | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3CCCH3CH3OH       |
| Third overtone C-H comparison       | tert-Butanol                       | C4H10O            | 75-65-0    | —  | —  | H3CCCH3CH3OH       |
| Ether                               | 1,1-dimethoxy-Ethane               | C4H10O2           | 534-15-6   | 111  | 157  | H3COCHCH3OCH3      |
| Butanediol series                   | 1,2-Butanediol                     | C4H10O2           | 584-03-2   | 110  | 156, 199                                     | HOCH2CHOHCH2CH3    |
| Butanediol series                   | 1,3-Butanediol                     | C4H10O2           | 107-88-0   | 110  | 156, 199                                     | HOCH2CH2CHOHCH3    |
| Butanediol series                   | 1,4-Butanediol                     | C4H10O2           | 110-63-4   | 110  | 156, 199                                     | HOCH2CH2CH2CH2OH   |
| Alcohol (diol)                      | 2,3-Butanediol                     | C4H10O2           | 513-85-9   | 109, 196                                     | 155, 198, 199                                | HOCHCH3CHOHCH3     |
| Butanediol series                   | 2,3-Butanediol                     | C4H10O2           | 513-85-9   | 110  | 156  | HOCHCH3CHOHCH3     |
| Ether                               | 2-ethoxy-Ethanol                   | C4H10O2           | 110-80-5   | 112  | 158  | H3CCH2OCH2CH2OH    |
| Four-carbon (butyl) comparison      | 2-ethoxy-Ethanol                   | C4H10O2           | 110-80-5   | 116  | 162  | H3CCH2OCH2CH2OH    |
| X-H compound comparison             | 2-Butanethiol (C-SH)               | C4H10S            | 513-53-1   | 130  | 176  | H3CCH2CHSHCH3      |
| X-H compound comparison             | 1-Butanamine (C-NH)                | C4H11N            | 109-73-9   | 130  | 176  | H3CCH2CH2CH2NH2    |
| Cyclic ether                        | Furan                              | C4H4O             | 110-00-9   | 141  | 187  | HCCHCHCHO          |
| Heterocyclic compound               | Furan                              | C4H4O             | 110-00-9   | 144  | 190  | HCCHCHCHO          |
| Acid vs. amide vs. ester comparison | Acetic acid                        | C4H4O2            | 64-19-7    | 142  | 188  | H3CCOOH            |
| Carboxylic acid                     | Acetic acid                        | C4H4O2            | 64-19-7    | 218  | 219  | H3CCOOH            |
| Aromatic compound with N or S       | Thiophene                          | C4H4S             | 110-02-1   | 136  | 182  | HCCHCHCHS          |
| Heterocyclic compound               | Thiophene                          | C4H4S             | 110-02-1   | 144  | 190  | HCCHCHCHS          |
| Alkyne                              | 2-Butyne                           | C4H6              | 503-17-3   | 129  | 175  | H3CCCH3            |
| Polyfunctional comparison           | 2-Butenal                          | C4H6O             | 123-73-9   | 117  | 163  | H3CCHCHCHO         |
| Ether                               | ethoxy-Ethyne                      | C4H6O             | 927-80-0   | 112  | 158  | H3CCH2OCCCH        |
| Four-carbon (butyl) comparison      | ethoxy-Ethyne                      | C4H6O             | 927-80-0   | 116  | 162  | H3CCH2OCCCH        |
| Heterocyclic (5-member ring)        | 4,5-dihydro-2(methylthio)-Thiazole | C4H7NS2           | 19975-56-5 | 145  | 191  | H3CSCNCH2CH2S      |
| Ketone                              | 2-Butanone                         | C4H8O             | 78-93-3    | 202  | 162, 203                                     | H3CCOCH2CH3        |
| Four-carbon (butyl) comparison      | 2-Butanone                         | C4H8O             | 78-93-3    | 116  | —  | H3CCOCH2CH3        |

(continued)

| Functional Group                | Compound Name             | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula |
|---------------------------------|---------------------------|-------------------|------------|--|--|--------------------|
| Aldehyde                        | Butanal                   | C4H8O             | 123-72-8   | 114, 204                                     | 160, 205                                     | H3CCH2CH2CHO       |
| Ether                           | ethoxy-Ethene             | C4H8O             | 109-92-2   | 112  | 158  | H2CCHOCH2CH3       |
| Four-carbon (butyl) comparison  | ethoxy-Ethene             | C4H8O             | 109-92-2   | 116  | —  | H2CCHOCH2CH3       |
| Pentanol series                 | 2-Butene-1,4-diol         | C4H8O2            | 110-64-5   | 113  | 159  | HOCH2CHCHCH2OH     |
| Four-carbon (butyl) comparison  | Butanoic acid             | C4H8O2            | 107-92-6   | 116  | 162  | H3CCH2CH2COOH      |
| Ether                           | ethoxy-Acetic acid        | C4H8O3            | 627-03-2   | 112  | 158  | H3CCH2OCH2COOH     |
| Butyl comparison group          | 2-bromo-Butane            | C4H9Br            | 78-76-2    | 120  | 166  | H3CCH2CHBrCH3      |
| Butyl comparison group          | 1-chlorobutane            | C4H9Cl            | 109-69-3   | 120  | 166  | H3CCH2CH2CH2Cl     |
| Butyl comparison group          | 2-chloro-Butane           | C4H9Cl            | 78-86-4    | 120  | 166  | H3CCHClCH2CH3      |
| Butyl comparison group          | 2-iodo-Butane             | C4H9I             | 513-48-4   | 120  | 166  | H3CCHICH2CH3       |
| Amide                           | N-methyl-Propanamide      | C4H9NO            | 1187-58-2  | 134  | 180  | H3CNHCOCH2CH3      |
| Amides, comparison group        | N-methyl-Propanamide      | C4H9NO            | 1187-58-2  | —  | 180  | H3CNHCOCH2CH3      |
| Alkene                          | 1-Pentene                 | C5H10             | 109-67-1   | 127  | 172  | H2CCHCH2CH2CH3     |
| Alkene, internal vs. terminal   | 2-methyl-2-Butene         | C5H10             | 513-35-9   | 128  | 174  | H3CCHCCH3CH3       |
| Alkane                          | Cyclopentane              | C5H10             | 287-92-3   | 121  | —  | CH2CH2CH2CH2CH2    |
| Alkane & cycloalkane comparison | Cyclopentane              | C5H10             | 287-92-3   | 121  | 167  | CH2CH2CH2CH2CH2    |
| Ketone                          | 2-Pentanone               | C5H10O            | 107-87-9   | 202  | 203  | H3CCOCH2CH2CH3     |
| Pentanol series                 | Cyclopentanol             | C5H10O            | 96-41-3    | 113  | 159  | HOCHCH2CH2CH2CH2   |
| Aldehyde                        | Pentanal                  | C5H10O            | 110-62-3   | 114  | 160  | H3CCH2CH2CH2CHO    |
| Cyclic ether                    | Tetrahydro-2H-Pyran       | C5H10O            | 142-68-7   | 141  | 187  | CH2CH2CH2CH2CH2O   |
| Carboxylic acid                 | Pentanoic acid            | C5H10O2           | 109-52-4   | —  | —  | H3CCH2CH2CH2COOH   |
| Heterocyclic (5-member ring)    | 2,2-dimethyl-Thiazolidine | C5H11NS           | 19351-18-9 | 145  | 191  | H3CCH3CNHCH2CH2S   |
| Alkane                          | Pentane                   | C5H12             | 109-66-0   | 119  | 165  | H3CCH2CH2CH2CH3    |
| Isomerism comparison group      | Pentane                   | C5H12             | 109-66-0   | 123  | 169  | H3CCH2CH2CH2CH3    |
| X-H compound comparison         | Pentane (C-C-H)           | C5H12             | 109-66-0   | 130  | 176  | H3CCH2CH2CH2CH3    |
| Pentanol series                 | 1-Pentanol                | C5H12O            | 71-41-0    | 113  | 159  | HOCH2CH2CH2CH2CH3  |
| Pentanol series                 | 2-Pentanol                | C5H12O            | 6032-29-7  | 113  | 159  | H3CCHOHCH2CH2CH3   |
| Alcohol (mono-OH)               | 3-Pentanol                | C5H12O            | 584-02-01  | 108, 197                                     | 154  | H3CCH2CHOHCH2CH3   |
| Pentanol series                 | 3-Pentanol                | C5H12O            | 584-02-1   | —  | 159  | H3CCH2CHOHCH2CH3   |
| Ether                           | 2,2-dimethoxy-Propane     | C5H12O2           | 77-76-9    | 111, 200                                     | 157, 201                                     | H3COCCH3CH3OCH3    |
| Alcohol (diol)                  | 2,4-Pentanediol           | C5H12O2           | 625-69-4   | 109  | 155  | H3CCHOHCH2CHCH3OH  |
| Ether                           | 1,1,2-trimethoxy-Ethane   | C5H12O3           | 24332-20-5 | 111, 200                                     | 157, 201                                     | H3COCHCH2OCH3OCH3  |
| Heterocyclic compound           | 2-bromo-Pyridine          | C5H4BrN           | 109-04-6   | 144  | 190  | NCBrCHCHCHCH       |

| Functional Group                    | Compound Name                 | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula   |
|-------------------------------------|-------------------------------|-------------------|------------|--|--|----------------------|
| Polyfunctional comparison           | 2-Furanmethanol               | C5H6O2            | 98-00-0    | 117  | 163  | HOCH2COCHCHCH        |
| Aromatic compound with N or S       | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 136  | 182  | H3CNCHCHCHCH         |
| Heterocyclic compound               | 1-methyl-1H-Pyrrole           | C5H7N             | 96-54-8    | 144  | 190  | H3CNCHCHCHCH         |
| Alkyne                              | 1-Pentyne                     | C5H8              | 627-19-0   | 129, 214                                     | 175, 215                                     | H3CCH2CH2CCH         |
| Polyene                             | 2-methyl-1,3-Butadiene        | C5H8              | 78-79-5    | 147  | 193  | H2CCCH3CHCH2         |
| Cycloalkene                         | Cyclopentene                  | C5H8              | 142-29-0   | 126  | 173  | HCCHCH2CH2CH2        |
| Cyclic ether                        | 3,4-dihydro-2H-Pyran          | C5H8O             | 110-87-2   | 141  | 187  | OCHCHCH2CH2CH2       |
| Polyfunctional comparison           | 3-methyl-2-Butenal            | C5H8O             | 107-86-8   | 117  | 163  | H3CCCH3CHCHO         |
| Acid vs. amide vs. ester comparison | 1-Propen-2-ol acetate         | C5H8O2            | 108-22-5   | 142  | 188  | H3CCOOCCH3CH2        |
| Cyclic ether                        | tetrahydro-4H-Pyran-4-one     | C5H8O2            | 29943-42-8 | 141  | 187  | OCCH2CH2OCH2CH2      |
| Amide                               | N,N-dimethyl-2-Propenamide    | C5H9NO            | 2680-03-7  | 133  | 179  | H2CCHCONCH3CH3       |
| Amino acid                          | N-formyl-Glycine, ethyl ester | C5H9NO3           | 3154-51-6  | 135  | 181  | HCONHCH2COOCH2CH3    |
| Polyene                             | 1,5-Hexadiene                 | C6H10             | 592-42-7   | 147, 220                                     | 193, 221                                     | H2CCHCH2CH2CHCH3     |
| Cycloalkene                         | Cyclohexene                   | C6H10             | 110-83-8   | 126  | 173  | HCCHCH2CH2CH2CH2     |
| Aryl vs. alkyl series               | Cyclohexene                   | C6H10             | 110-83-8   | 137  | 183  | HCCHCH2CH2CH2CH2     |
| Ketone                              | Cyclohexanone                 | C6H10O            | 108-94-1   | 115, 202                                     | 161, 203                                     | OCCH2CH2CH2CH2CH2    |
| Alkene                              | 1-Hexene                      | C6H12             | 592-41-6   | 127  | 172  | H2CCHCH2CH2CH2CH3    |
| Alkene, internal vs. terminal       | 2,3-dimethyl-2-Butene         | C6H12             | 563-79-1   | 128  | 174  | H3CCCH3CCH3CH3       |
| Alkene, internal vs. terminal       | 3,3-dimethyl-1-Butene         | C6H12             | 558-37-2   | 128  | 174  | H2CCHCCH3CH3CH3      |
| Alkane                              | Cyclohexane                   | C6H12             | 110-82-7   | 121, 206                                     | —  | CH2CH2CH2CH2CH2CH2   |
| Alkane & cycloalkane comparison     | Cyclohexane                   | C6H12             | 110-82-7   | 121  | 167  | CH2CH2CH2CH2CH2CH2   |
| Aryl vs. alkyl series               | Cyclohexane                   | C6H12             | 110-82-7   | 137, 206, 207                                | 183, 208, 209                                | CH2CH2CH2CH2CH2CH2   |
| Alkane                              | Methylcyclopentane            | C6H12             | 96-37-7    | 121  | —  | H3CCHCH2CH2CH2CH2    |
| Alkane & cycloalkane comparison     | Methylcyclopentane            | C6H12             | 96-37-7    | 121  | 167  | H3CCHCH2CH2CH2CH2    |
| Ketone                              | 2-Hexanone                    | C6H12O            | 591-78-6   | 115  | 161  | H3CCOCH2CH2CH2CH2    |
| Ketone                              | 3-Hexanone                    | C6H12O            | 589-38-8   | 115  | 161  | H3CCH2CH2COCH2CH2    |
| Functional group comparisons        | 3-Hexanone                    | C6H12O            | 589-38-8   | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3CCH2CH2COCH2CH2    |
| Aldehyde                            | Hexanal                       | C6H12O            | 66-25-1    | —  | 160  | H3CCH2CH2CH2CH2CHO   |
| Acid vs. amide vs. ester comparison | 2-ethoxy-acetate-Ethanol      | C6H12O3           | 111-15-9   | 142  | 188  | H3CCOOCCH2CH2OCH2CH3 |
| Isomerism comparison group          | 2-methylpentane               | C6H14             | 107-83-5   | 123  | 169  | H3CCH2CH2CHCH3CH3    |
| Alkane                              | Hexane                        | C6H14             | 110-54-3   | 119  | —  | H3CCH2CH2CH2CH2CH3   |

(continued)

| Functional Group                | Compound Name                           | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula      |
|---------------------------------|---|-------------------|------------|--|--|-------------------------|
| Ether                           | 1,2-diethoxy-Ethane                     | C6H14O2           | 629-14-1   | 111  | 157  | H3CCH2OCH2CH2OCH2CH3    |
| Alcohol (diol)                  | 2,5-Hexanediol                          | C6H14O2           | 2935-44-6  | 109  | 155  | H3CCHOHCH2CH2CHCH3OH    |
| Amide                           | Hexamethyl-phosphoric triamide          | C6H18N3OP         | 680-31-9   | 133  | 179  | H3CNCH3PONCH3CH3NCH3CH3 |
| Aromatic (aryl) compound        | 2,4,5-trichloro-Phenol                  | C6H3Cl3O          | 95-95-4    | 139  | 185  | ClCCClCCHClCClCOHCH     |
| Aromatic (aryl) compound        | bromo-Benzene                           | C6H5Br            | 108-86-1   | 140  | 186  | BrCCHCHCHCHCHCH         |
| Aromatic (aryl) compound        | nitro-Benzene                           | C6H5NO2           | 98-95-3    | 140  | 186  | O2NCCHCHCHCHCHCH        |
| Aryl vs. alkyl series           | Benzene                                 | C6H6              | 71-43-2    | 138, 206, 207                                | 184, 208, 209                                | CHCHCHCHCHCHCH          |
| Functional group comparisons    | Benzene                                 | C6H6              | 71-43-2    | 146  | 192  | CHCHCHCHCHCHCH          |
| Aryl amine                      | 4-methyl-Pyridine                       | C6H7N             | 108-89-4   | 132  | 178  | H3CCCHCHNCHCHCH         |
| Aromatic compound with N or S   | 4-methyl-Pyridine                       | C6H7N             | 108-89-4   | 136  | 182  | H3CCCHCHNCHCHCH         |
| Aryl amine                      | Benzenamine (Aniline)                   | C6H7N             | 62-53-3    | 132  | 178  | H2NCCHCHCHCHCHCH        |
| Aryl amine                      | 2-Pyridinemethanol                      | C6H7NO            | 586-98-1   | 132  | 178  | HOCH2CNCHCHCHCHCH       |
| Polyene                         | 1,3-Cyclohexadiene                      | C6H8              | 592-57-4   | 147  | 193  | HCCHCHCHCH2CH2          |
| Ketone                          | 2-Cyclohexen-1-one                      | C6H8O             | 930-68-7   | 115  | 161  | OCCHCHCH2CH2CH2         |
| Heterocyclic (5-member ring)    | 4,5-dihydro-2-(2-propenylthio)-Thiazole | C6H9NS2           | 3571-74-2  | 145  | 191  | H2CCHCH2SCNCH2CH2S      |
| Amide                           | N, N-dimethyl-3-oxo-Butanamide          | C6H11NO2          | 2044-64-6  | 134  | 180  | (H3C)2NCOCH2COCH3       |
| Alkyne                          | 1-Heptyne                               | C7H12             | 628-71-7   | 214  | 215  | HCCCH2CH2CH2CH2CH2CH3   |
| Cycloalkene                     | Cycloheptene                            | C7H12             | 628-92-2   | 126  | 173  | HCCHCH2CH2CH2CH2CH2     |
| Alkene                          | 1-Heptene                               | C7H14             | 592-76-7   | 210  | 211  | H2CCHCH2CH2CH2CH2CH3    |
| Alkane                          | Cycloheptane                            | C7H14             | 291-64-5   | 121  | —  | H2CCH2CH2CH2CH2CH2CH2   |
| Alkane & cycloalkane comparison | Cycloheptane                            | C7H14             | 291-64-5   | 121  | 167  | H2CCH2CH2CH2CH2CH2CH2   |
| Aldehyde                        | Heptanal                                | C7H14O            | 111-71-7   | 114, 204                                     | 205  | H3CCH2CH2CH2CH2CH2CHO   |
| Alkane                          | Heptane                                 | C7H16             | 142-82-5   | —  | 165  | H3CCH2CH2CH2CH2CH2CH3   |
| Isomerism comparison group      | Heptane                                 | C7H16             | 142-82-5   | 123  | 169  | H3CCH2CH2CH2CH2CH2CH3   |
| Alkyl amine                     | 1,7-Heptanediamine                      | C7H18N2           | 646-19-5   | 131  | 177  | H2N(CH2)7NH2            |
| Aldehyde, substituted aromatic  | 2-bromo-Benzaldehyde                    | C7H5BrO           | 6630-33-7  | 118  | 164  | HOCCBrCHCHCHCH          |
| Aldehyde, substituted aromatic  | 2-chloro-Benzaldehyde                   | C7H5ClO           | 89-98-5    | 118  | 164  | HOCCClCHCHCHCH          |
| Aldehyde, substituted aromatic  | Benzaldehyde                            | C7H6O             | 100-52-7   | 118  | 164  | HOCCCHCHCHCHCH          |
| Aryl vs. alkyl series           | Benzaldehyde                            | C7H6O             | 100-52-7   | 138  | 184  | HOCCCHCHCHCHCH          |
| Polyene                         | 1,3,5-Cycloheptatriene                  | C7H8              | 544-25-2   | 147  | 193  | HCCHCHCHCH2CHCH         |



| Functional Group              | Compound Name                              | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula   |
|-------------------------------|--|-------------------|------------|--|--|----------------------|
| Aryl vs. alkyl series         | methyl-Benzene                             | C7H8              | 108-88-3   | 138  | 184  | H3CC(CH)5            |
| Aromatic (aryl) compound      | methyl-Benzene                             | C7H8              | 108-88-3   | 140  | 186  | H3CC(CH)5            |
| Functional group comparisons  | methyl-Benzene                             | C7H8              | 108-88-3   | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3CC(CH)5            |
| Third overtone C-H comparison | Toluene                                    | C7H8              | 108-88-3   | —  | —  | H3CC(CH)5            |
| Aromatic (aryl) compound      | 3-methyl-Phenol                            | C7H8O             | 108-39-4   | 139  | 185  | HOCCCHCH3CHCHCH      |
| Aromatic (aryl) compound      | 4-methyl-Phenol                            | C7H8O             | 106-44-5   | 140  | 186  | H3CCCHCHCOHCHCH      |
| Ether                         | methoxy-Benzene                            | C7H8O             | 100-66-3   | 111, 200                                     | 157, 201                                     | H3COC(CH)5           |
| Heterocyclic compound         | 3-ethyl-Pyridine                           | C7H9N             | 536-78-7   | 144  | 190  | NCHCCH2CH3CHCHCH     |
| Aromatic (aryl) compound      | 1,2-dimethyl-Benzene<br>( <i>o</i> -Xylol) | C8H10             | 95-47-6    | 139  | —  | H3CCCCH3(CH)4        |
| Aromatic (aryl) compound      | 1,3-dimethyl-Benzene<br>( <i>m</i> -Xylol) | C8H10             | 108-38-3   | —  | 185  | H3CCHCCH3(CH)3       |
| Aromatic (aryl) compound      | 1,4-dimethyl-Benzene<br>( <i>p</i> -Xylol) | C8H10             | 106-42-3   | 139  | 185  | H3CCHCHCCH3CHCH      |
| Aromatic (aryl) compound      | 2-ethyl-Phenol                             | C8H10O            | 90-00-6    | 139  | 185  | HOCCCH2CH3(CH)4      |
| Ether                         | 2-phenoxy-Ethanol                          | C8H10O2           | 122-99-6   | 112  | 158  | HOCH2CH2OC(CH)5      |
| Polyene                       | 1,3-Cyclooctadiene                         | C8H12             | 1700-10-3  | 147  | 193  | HCCHCHCH(CH2)4       |
| Aryl amine                    | N,N-dimethyl-1,3-Benzenediamine            | C8H12N2           | 2836-04-2  | 132  | 178  | N(CH3)2CCHCNH2(CH)3  |
| Aryl vs. alkyl series         | 1,7-Octadiene                              | C8H14             | 3710-30-3  | 137  | 183  | H2CCH(CH2)4CHCH2     |
| Polyene                       | 1,7-Octadiene                              | C8H14             | 3710-30-3  | 220  | 221  | H2CCH(CH2)4CHCH2     |
| Alkyne                        | 1-Octyne                                   | C8H14             | 629-05-0   | 129, 214                                     | 175, 215                                     | HCC(CH2)5CH3         |
| Alkyne                        | 4-Octyne                                   | C8H14             | 1942-45-6  | 129  | 175  | H3CCH2CH2CCCH2CH2CH3 |
| Cycloalkene                   | Cyclooctene                                | C8H14             | 931-87-3   | 126  | 173  | HCCH(CH2)6           |
| Amides, comparison group      | N,N-dimethyl-3-oxo-Butanamide              | C8H15NO2          | 2235-46-3  | —  | 180  | OCCH3CH2CON(CH2CH3)2 |
| Alkene                        | 1-Octene                                   | C8H16             | 111-66-0   | 127  | 172  | H2CCH(CH2)5CH3       |
| Isomerism comparison group    | 2,2,4-trimethylpentane                     | C8H18             | 540-84-1   | 123, 206                                     | 169, 207                                     | (H3C)3CCH2CH(CH3)2   |
| Aryl vs. alkyl series         | 2,2,4-trimethyl-Pentane                    | C8H18             | 540-84-1   | 137  | 183  | (H3C)3CCH2CH(CH3)2   |
| Functional group comparisons  | 2,2,4-trimethyl-Pentane                    | C8H18             | 540-84-1   | 107, 146, 222, 223                           | 153, 192, 224, 225                           | (H3C)3CCH2CH(CH3)2   |
| Alkane                        | Octane                                     | C8H18             | 111-65-9   | 119  | 165  | H3C(CH2)6CH3         |
| Aryl vs. Alkyl Series         | Octane                                     | C8H18             | 111-65-9   | 137, 206, 207                                | 183, 208, 209                                | H3C(CH2)6CH3         |
| Third overtone C-H comparison | Trimethyl pentane                          | C8H18             | 540-84-1   | —  | —  | (H3C)3CCH2CH(CH3)2   |
| Alkyl amine                   | N,N,N',N'-tetramethyl-1,4-Butanediamine    | C8H20N2           | 111-51-3   | 131  | 177  | H3CNCH3(CH2)4N(CH3)2 |

(continued)

| Functional Group               | Compound Name                               | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula      |
|--------------------------------|---|-------------------|------------|--|--|-------------------------|
| Heterocyclic compound          | 1H-Indole                                   | C8H7N             | 120-72-9   | 144  | 190  | HNCHCHC(CH)4C           |
| Aryl amine                     | Indole, 1-H                                 | C8H7N             | 120-72-9   | 132  | 178  | HNCHCHC(CH)4C           |
| Aromatic compound with N or S  | Indole, 1H-                                 | C8H7N             | 120-72-9   | 136  | 182  | HNCHCHC(CH)4C           |
| Carboxylic acid                | Methyl ester-Benzonic acid                  | C8H8O2            | 93-58-3    | 143  | 189  | H3COCOC(CH)5            |
| Aldehyde, substituted aromatic | 2,4-dimethyl-Benzaldehyde                   | C9H10O            | 15764-16-6 | 118  | 164  | HCOCCH3CHCCH3(CH)2      |
| Polyfunctional comparison      | Benzenepropanal                             | C9H10O            | 104-53-0   | 117  | 163  | OCHCH2CH2C(CH)5         |
| Alkene                         | 1-Nonene                                    | C9H18             | 124-11-8   | 210  | 211  | H3C(CH2)6CHCH2          |
| Alkyl amine                    | N,N-dipropyl-1-Propanamine                  | C9H21N            | 102-69-2   | 131  | 177  | (H3CCH2CH2)3N           |
| Aromatic compound with N or S  | Quinoline                                   | C9H7N             | 91-22-5    | 136  | 182  | NC(CH)4C(CH)3           |
| Heterocyclic compound          | Quinoline                                   | C9H7N             | 91-22-5    | 144  | 190  | NC(CH)4C(CH)3           |
| Polyfunctional comparison      | 3-phenyl-2-Propenal                         | C9H8O             | 14371-10-9 | 117  | 163  | OCHCHCHC(CH)5           |
| Aldehyde, Substituted Aromatic | 2,4,6-trimethyl-Benzaldehyde                | C10H12O           | 487-68-3   | 118  | 164  | HCOCCH3CHCCH3CHCCH3     |
| Alkene                         | 1-Decene                                    | C10H20            | 872-05-9   | 127, 210                                     | 172, 211                                     | H2CCH(CH2)7CH3          |
| Aldehyde                       | Decanal                                     | C10H20O           | 112-31-2   | 114, 204                                     | 160, 205                                     | OCH(CH2)8CH3            |
| Carboxylic acid                | Decanoic acid                               | C10H20O2          | 334-48-5   | —  | 219  | HOCO(CH2)8CH3           |
| Amino acid                     | D-Valine, 3-methyl, 1,1-dimethylethyl ester | C10H21NO2         | 61169-85-5 | 135  | 181  | (H3C)3COCOCHNH2C(CH3)3  |
| Amino acid                     | L-Valine, 3-methyl, 1,1-dimethylethyl ester | C10H21NO2         | 31556-74-8 | 135  | 181  | (H3C)3COCOCHNH2C(CH3)3  |
| Third overtone C-H comparison  | n-Decane                                    | C10H22            | 124-18-5   | —  | —  | H3C(CH2)8CH3            |
| Alkyl Amine                    | 1-Decanamine                                | C10H23N           | 2016-57-1  | 131, 212                                     | 177, 213                                     | H3C(CH2)9NH2            |
| Functional group comparisons   | 1-Decanamine                                | C10H23N           | 2016-57-1  | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3C(CH2)9NH2            |
| Aromatic (aryl) compound       | Naphthalene                                 | C10H8             | 91-20-3    | 140  | 186  | C(CH)4C(CH)4            |
| Alkane                         | Undecane                                    | C11H24            | 1120-21-4  | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3C(CH2)9CH3            |
| Functional group comparisons   | Undecane                                    | C11H24            | 1120-21-4  | 107, 146, 222, 223                           | 153, 192, 224, 225                           | H3C(CH2)9CH3            |
| Aromatic (aryl) compound       | 1,1-Biphenyl                                | C12H10            | 92-52-4    | 139  | 185  |                         |
| Amide                          | N, N-dimethyl-3-methyl-Benzamide            | C12H17NO          | 134-62-3   | —  | 180  | (H3CCH2)2NCOCCHCH3(CH)3 |
| Carboxylic acid                | Dodecanoic acid                             | C12H24O2          | 143-07-7   | 143, 218                                     | 189  | (CH)5CC(CH)5            |
| Alkyl amine                    | Cyclododecanamine                           | C12H25N           | 1502-03-0  | 131, 212                                     | 177, 213                                     | H2NCH(CH2)11            |
| Alkane                         | Dodecane                                    | C12H26            | 112-40-3   | 119  | 165  | H3C(CH2)10CH3           |
| Aromatic (aryl) compound       | Phenanthrene                                | C14H10            | 85-01-8    | 140  | 186  | C(CH)4C(CH)2C(CH)4C     |

| Functional Group | Compound Name   | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula                 |
|------------------|---|-------------------|------------|--|--|------------------------------------|
| Carboxylic acid  | Benzoic acid anhydride                                      | C14H10O3          | 93-97-0    | 218  | 219  | C(CH)5COOCOC(CH)5                  |
| Alkene           | 1-Tetradecene   | C14H28            | 1120-36-1  | 127  | 172  | H3C(CH2)11CHCH2                    |
| Alkane           | Octadecane  | C18H38            | 593-45-3   | 119  | 165  | H3C(CH2)16CH3                      |
| Polymers         | 60% polypropylene and 40% polyester                         | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | 60% polypropylene-polyethylene acopolymer and 40% polyester | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Atactic polypropylene                                       | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Cellulose acetate   | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Cellulose acetate butyrate                                  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Cellulose propionate  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Ethyl cellulose   | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Ethylene vinyl acetate                                      | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(ethylene oxide)  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(isobutyl methacrylate)                                 | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(vinyl butyral)   | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(vinyl chloride)  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(vinyl pyrrolidone)                                     | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(vinyl stearate)  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Poly(vinylidene fluoride)                                   | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Polyacrylic acid  | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Polyethylene, chlorinated (25% Cl)                          | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Polypropylene, isotactic, chlorinated                       | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |
| Polymers         | Polystyrene   | Polymer           | N/A        | —  | —  | See Chapter 12: Synthetic Polymers |

(continued)

| Functional Group   | Compound Name                           | Molecular Formula | CAS Number | 10500–6300 cm <sup>-1</sup><br>(952–1587 nm) | 7200–3800 cm <sup>-1</sup><br>(1389–2632 nm) | Structural Formula                    |
|--|---|-------------------|------------|--|--|---------------------------------------|
| Polymers   | Silicone                                | Polymer           | N/A        | —  | —  | See Chapter 12:<br>Synthetic Polymers |
| Polymers   | Starch                                  | Polymer           | N/A        | —  | —  | See Chapter 12:<br>Synthetic Polymers |
| Polymers   | Styrene isoprene<br>styrene             | Polymer           | N/A        | —  | —  | See Chapter 12:<br>Synthetic Polymers |
| Polymers   | Styrene, ethylene,<br>styrene copolymer | Polymer           | N/A        | —  | —  | See Chapter 12:<br>Synthetic Polymers |
| <i>Note:</i> N/A indicates natural or synthetic product with no designated CAS number. |   |                   |            |  |  |                                       |